

The Mixed Waste Management Facility

Technology Selection and Implementation Plan Part II: Support Processes

March 1995

Lawrence Livermore National Laboratory
Environmental Programs



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The Mixed Waste Management Facility

Technology Selection and Implementation
Plan Part II: Support Processes

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Mixed Waste Management Facility
Technology Selection and Implementation Plan

Part II

March 1995

Abstract

The purpose of this document is to establish the foundation for the selection and implementation of technologies to be demonstrated in the Mixed Waste Management Facility, and to select the technologies for initial pilot-scale demonstration. Criteria are defined for judging demonstration technologies, and the framework for future technology selection is established. On the basis of these criteria, an initial suite of technologies was chosen, and the demonstration implementation scheme was developed. Part I, previously released, addresses the selection of the primary processes. Part II addresses process support systems that are considered "demonstration technologies." Other support technologies, e.g., facility off-gas, receiving and shipping, and water treatment, while part of the integrated demonstration, use best available commercial equipment and are not selected against the demonstration technology criteria.

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Executive Summary

This document defines the basis for technology selection and implementation into the Mixed Waste Management Facility (MWMF), and establishes the technologies selected for initial demonstration. The MWMF is being designed as a test bed for the demonstration and evaluation of mixed waste treatment processes that will provide an effective and alternative treatment option where the current best demonstrated available technology (BDAT) is incineration. The MWMF Project will bridge mature, bench-scale demonstrated technologies with full-scale treatment facilities. The MWMF will have the capability to evaluate a variety of competing technologies on the same organic waste streams, and to define the waste streams best suited for specific treatment approaches.

The MWMF will be operated in an integrated manner, demonstrating state-of-the-art waste characterization, sorting, and feed preparation technologies, the best mature treatment systems, and the preparation of robust final forms. A networked instrumentation and control system covering process and supervisory control functions, monitoring, and safety interlocks will also be demonstrated. Data from the MWMF will provide the Department of Energy (DOE) and industry with engineering data for the design of full-size treatment plants, and provide the basis for permitting and Federal and State environmental documentation.

Two classes of equipment are defined: "demonstration technology" and best available commercial technology. The demonstration technologies are the key elements of the integrated treatment trains, which will be evaluated against the criteria established in this document. The MWMF Project will be responsible for selecting the initial demonstration technologies for inclusion in the pilot plant. Two categories of technologies are considered: primary process technologies, described in the previously released *Technology Selection and Implementation Plan Part I: Primary Processes*,* and process support technologies, described in this document. The primary process technologies are the process systems responsible for the destruction of the organic component of the waste stream. Process support technologies include feed characterization and preparation, transport and storage, off-gas treatment and final forms. Process support technologies to be demonstrated have been selected based on criteria described in this document.

* R. D. Streit and M. G. Adamson, *Technology Selection and Implementation Plan Part I: Primary Processes*, Lawrence Livermore National Laboratory, 1994, UCRL-ID-116210 Pt. 1.

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List of Acronyms

ALARA	as low as reasonably achievable (attainable)
ANL	Argonne National Laboratory
BACT	best available control technology
BDAT	best demonstrated available technology
CAT	computerized axial tomography
CRADA	cooperative research and development agreement
D&D	development and demonstration
DCO	direct chemical oxidation
DOE	Department of Energy
DRE	destruction efficiency
ES&H	Environment, Safety, & Health
FCCA	Federal Facilities Compliance Act
HEPA	high-efficiency particulate air (filtered)
HWM	hazardous waste management
INEL	Idaho National Engineering Laboratory
LANL	Las Alamos National Laboratory
LLMW	low-level mixed waste
LLNL	Lawrence Livermore National Laboratory
MEO	mediated electrochemical oxidation
MLLW	mixed, low-level waste
MSO	molten salt oxidation
MWMF	Mixed Waste Management Facility (at LLNL)
NDA	nondestructive analysis
NDE	nondestructive evaluation
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PNL	Pacific Northwest Laboratory
RCRA	Resource Conservation and Recovery Act
RFP	Rocky Flats Plant
RTR	real-time radiography
SAIC	Science Applications International Corporation
SCWO	super-critical water oxidation
SNL	Sandia National Laboratory
SRL	Savannah River Laboratory
TRZ	thermochemical reaction zone
UVP	ultraviolet photolysis
VOC	volatile organic compounds (contaminants)
WOX	wet oxidation
XOG	experimental off-gas

1. Introduction

Mixed waste is a growing national problem. Annual generation of mixed waste is estimated to be 30,000 m³, and an estimated 250,000 m³ of low-level mixed waste is currently in storage nationwide. Few acceptable treatment and disposal methods for mixed waste are currently available, resulting in increased storage requirements. Inadequate treatment capability could ultimately result in restriction or curtailment of programs within the Department of Energy (DOE). It is expected that without development of credible solutions for the disposal of these wastes, authority to store mixed waste under the Federal Facilities Compliance Act of 1992 (FFCA) will be jeopardized.

The Mixed Waste Management Facility (MWMF) at the Lawrence Livermore National Laboratory (LLNL) will be a national test bed for demonstrating technologies that are alternatives to incineration for the treatment of low-level radioactive, organic mixed waste. The MWMF will link mature, bench-scale-proven technologies with full-scale treatment facilities. The facility will house the capability to evaluate a variety of competing technologies on the same organic waste streams, and to define treatment approaches for specific waste streams.

In this document, we first briefly discuss the purpose and scope of the MWMF to provide background and the high-level basis for technology selection (Section 2). A more detailed discussion of the scope and objectives of the MWMF Project can be found in the *MWMF Project Plan*.^{*} Subsequently, we address the strategy for implementation of the initial suite of technologies and design basis operations (Section 3). We then present the criteria for the selection of the support process technologies, followed by a series of technology assessments. For each of the support processes evaluated, a very brief description of the technology and the purpose for demonstration in the MWMF is provided in Appendix A, in which the technology will be evaluated relative to the criteria and key issues will be identified. We present the results of the technology selection in Section 4.4.

^{*} Karin King, *MWMF Draft Final Project Plan*, RUST Geotech Inc., 1994, #P-GJPO-1626.

2. The Mixed Waste Management Facility

2.1 Purpose

The Mixed Waste Management Facility (MWMF) Project has been established to demonstrate integrated technologies for the treatment of low-level organic mixed waste at a pilot-plant scale. In response to the increasing public concerns regarding incineration as a treatment technology, this project will focus on demonstrating a variety of environmentally acceptable treatment processes that are equivalent to the best demonstrated available technology (BDAT); the current BDAT is incineration. In addition, the facility will be used to evaluate processes for the treatment of certain waste streams, e.g., aqueous organics, for which incineration is not an efficient solution. The facility will be used to evaluate these technologies relative to the Federal and State treatment standards that identify incineration as the BDAT.

By developing an infrastructure capable of supporting a full range of waste streams and treatment technologies, the MWMF will not be “locked” into one specific mixed-waste-remediation approach. The facility will be capable of demonstrating technologies as they emerge from bench-scale testing, as well as future technologies that are in early phases of research evaluation. The facility will be operated in an integrated manner, demonstrating state-of-the-art waste-characterization and feed-preparation technologies, the best mature treatment systems, and the preparation of robust ceramic final forms. The MWMF will provide DOE with engineering, operations, and cost data for the design of full-size treatment plants.

2.2 Scope of the MWMF

The MWMF Project will be responsible for selection, design, procurement, fabrication, installation, and activation of the initial suite of technologies. *Primary treatment* technologies to be demonstrated are those that have been sufficiently proven in laboratory and bench-scale experiments to be effective alternatives to incineration for the treatment of low-level organic mixed waste. *Support processes* to be demonstrated have the potential to provide full integration of the treatment system using technologies beyond those currently deployed for mixed-waste processing. The facility will integrate all phases of waste handling and treatment, including receiving and characterization, feed preparation and transport, treatment processes, and final forms preparation. The facility will incorporate a networked instrumentation and control system covering process and supervisory control functions, as well as safety and security interlocks.

In addition to developing an integrated mixed waste demonstration facility, a key element of the project scope is to lay a foundation for the subsequent permitting, Federal and State environmental documentation, and public participation. Industry involvement and technology transfer for design and deployment of a full-scale operating facility for the treatment of low-level organic mixed waste is an essential element of the project plan. The project will also be responsible for defining and implementing a

rigorous Environment, Safety, and Health (ES&H) program; for assuring that the success criteria for experimental technology results are in accordance with the broader programmatic objectives of DOE and LLNL; and for maintaining a quality assurance program to provide traceable and verifiable evidence of achievements.

3. Strategy for Technology Implementation and Waste Stream Selection

3.1 Implementation

The objective of the MWMF is to demonstrate integrated mixed waste processing technologies. The demonstration will stress the scale-up to near full scale, e.g., pilot scale, so as to qualify the integrated process for full-scale plant operation. The integrated demonstration means that all aspects of the treatment process are to be demonstrated: state-of-the-art waste characterization, sorting, and feed-preparation technologies; the best mature treatment systems; and the preparation of robust final forms. The primary chemical process, while an important component of this integration, is only a part of the fully integrated demonstration.

The infrastructure of the MWMF will be capable of supporting a wide range of waste streams and treatment technologies. The MWMF will not be “locked” into one specific mixed waste remediation approach. Each of these individual process and process support technologies selected for demonstration will provide a component of an overall integrated process train. As a key element of the demonstration, the integrated train will be evaluated against the BDAT specifications; for a specific waste stream, the integrated process will consist of a specific waste preparation, primary process treatment, and final forms. Although the initial operations will consider the primary process individually, future operations include the option to link primary processes in series or parallel to define alternative demonstration trains.

Data from the operation of the MWMF will provide DOE with engineering data for the design of full-size treatment plants. It will also benchmark information on the cost of installing and operating a mixed waste treatment facility in the 1990s and beyond. Further, a “blueprint” for successfully permitting mixed waste treatment facilities will also be established.

In the initial operation, the facility will be set up to process one waste stream at a time through one central process technology. Each process technology should be designed such that it may be shut down to allow for technology demonstrations from other waste processing trains. “Shut down” in this respect requires that no processing residues are being generated, or that such residues can be stored at the process until secondary support processing capacity is available.

3.2 Waste Stream Selection

The waste streams selected for treatment in the MWMF were chosen because they are representative of the DOE’s low-level combustible mixed waste inventory. The waste inventory, as reported in the Interim Mixed Waste Inventory Report (IMWIR),

Table 1. DOE's current inventory of low-level mixed waste.

WMIS no.	Description	Current inventor (m ³)	Organic component (m ³)
1000	Aqueous liquids	116,470	0
2000	Organic liquids	16,623	13,964
3000	Solid process residue	45,056	4,506
4000	Soils	9,930	993
5000	Debris	39,710	9,928
	Other	19,248	813
Totals		247,037	30,203

April 1993, is ~247,000 m³. The waste categories and inventory amounts are summarized in Table 1. It is estimated that ~88% of the total volume contains some hazardous organic contaminants. Incineration is currently listed as the BDAT for these waste streams.

However, of the total volume of waste, organics comprise about 30,000 m³, or 12%. This is shown in the last column of Table 1. The large discrepancy between the 12% and 88% is due to the large inorganic constituent in the matrix of the waste, such as soil, salt, sludges, and debris. The inorganic component in the waste can be separated and stabilized in a final form, such as grout, glass, or polymer microencapsulation. It is the organic components in the DOE's waste—organic liquids, organic solids, and condensed liquids and gases after thermal desorption—as well as the aqueous/organic liquid streams that are of interest for treatment in the MWMF.

The mission of the MWMF is to test alternatives to the use of incineration for destroying the organic constituent of the waste and possibly to declare them BDATs in place of or along side incineration. The streams selected for treatment in the MWMF include aqueous liquids, organic liquids, combustible solids, and scintillation cocktails. The organic liquids to be treated include halogenated and nonhalogenated solvents, oils, etc. The combustible solids include paper, cloth, plastics, and heterogeneous wastes contaminated with hazardous liquids and/or metals. Table 2 summarizes the waste streams selected for initial MWMF operations.

Although waste streams that have a high inorganic component are not specifically selected to be treated in the MWMF, MWMF technologies should be capable of destroying the organic contaminant that would be present in such streams. Thus the technologies selected for demonstration in the MWMF may be viewed as an integral part, i.e., the primary treatment technologies, of a complete waste-treatment train that includes pretreatment, primary treatment, and post-treatment.

The MWMF demonstration also includes the treatment of aqueous waste streams that are not incinerable but are a component of the DOE inventory and may be generated in a full-scale waste treatment plant. These aqueous streams include both halogenated and nonhalogenated organics in water. The actual aqueous streams selected for treatment in the MWMF contain the following organic contaminants: Trimsol (a cutting oil), vacuum pump oils, waste oils, benzene, toluene, and other nonhalogenated solvents.

Table 2. Waste streams selected for initial MWMF operations.

Code no.	Category Title	Description
1300	Neutral aqueous liquids	Neutral aqueous solutions ($2 < \text{pH} < 12.5$) having less than 1% organic content. May contain pumpable inert solids up to 35–40% of the mass (e.g., very dilute Trimsol water.)
2110	Aqueous/halogenated organic liquids	Liquid streams containing mixtures of aqueous and halogenated organic liquids with 1–99% organic content. Typical organic constituents are PCE, TCE, TCA, and Trimsol constituents.
2120	Aqueous/non-halogenated organic liquids	Liquid streams containing mixtures of aqueous and nonhalogenated organic liquids with 1–99% organic content. Typical organic constituents are heavy hydrocarbons, oils, and solvents (e.g., xylene, toluene, benzene).
2210	Halogenated organic liquids	Nearly pure organic liquids containing more than trace levels of halogens (>1000 ppm of F, Cl, Br, etc.). Typical organic constituents are TCE, PCE, and TCA.
2220	Nonhalogenated organic liquids	Nearly pure organic liquids free of more than trace levels of halogens (<1000 ppm of F, Cl, Br, etc.). Typically comprised of organic oils (heavy hydrocarbons).
5310	Combustible debris/plastics and rubber	Plastic and rubber such as sheeting, containers, gloves, gaskets, and components of benelex or Plexiglass.
5312	Combustible debris/halogenated plastics	Plastics containing halogens as part of their chemical structure, such as PVC.
5330	Combustible debris/paper and cloth	Paper and cloth items, such as protective clothing, and items used to wipe up contamination or absorb liquids. Wipes may contain some absorbed organic and aqueous liquids. Principal constituents are “cellulosics.”
5440	Heterogeneous debris/predominantly combustible	Debris materials containing $>50\%$ combustible materials with other non-combustible debris.
6140	Scintillation cocktails	Solutions used for scintillation counting. Solutions are most often in the original glass or plastic analysis bottles. They are made up of approximately 85% assorted proprietary organics, 5% methanol, and 10% water.

4. Support Process Technology Selection

4.1 Strategy for Selection

Support process technologies will be selected for the Mixed Waste Management Facility (MWMF) on the basis of criteria described in this section. The technologies will be evaluated and categorized in one of three groups: selected for demonstration, selected for potential future demonstration, or rejected as a demonstration unit within the MWMF. The selection of technology will be the responsibility of the LLNL MWMF Project Manager, in consultation with the Project Scientific Advisory Committee and the Scientific Requirements Staff. Final selection will be approved by the DOE.

The selection of technologies for demonstration in the MWMF is part of the continuing operations of the facility. The criteria, as defined in the subsequent section, should be reviewed on a regular basis (no longer than biannually) to assure appropriateness to the requirements and needs of the DOE. As the criteria or their relative importance change, or as new data are obtained, the selection of primary or secondary process technologies may be modified.

After a support processes technology has been selected, it will be maintained as the baseline. Processes will be reevaluated at key project milestones (e.g., Preliminary Design Review) to ensure that they are appropriate and continue to meet selection criteria. If a technology is not ready for demonstration, or the criteria have changed significantly from the time of selection, a change to a backup technology may be appropriate.

4.2 Criteria for Process Support Technology Selection

Several criteria need to be considered in order to evaluate the process support technologies. The primary function of the process support technologies is to provide for full integration of the treatment process. The integration will include waste receiving and characterization; feed preparation and transport; final disposition of the waste processing outputs, off-gas, water, and solid residues; and an instrumentation and control system for integrated material tracking, facility safety, and coordinated control. A number of these process support elements have been selected as “demonstration technologies” as discussed in subsequent sections. The criteria for selection are intended to lead to a suite of process support technologies capable of (1) handling and treating identified DOE low-level radioactive, organic mixed waste; (2) providing for personnel safety; and (3) demonstrating the complete integration of the process train. Following is a list of the criteria for selection of support process technologies.

Appropriateness for MWMF

The process support technologies should be appropriate for the feeds (including surrogate and actual mixed waste), primary processes, and residues expected from

destruction of the representative mixed-waste streams. In particular, the support processes must provide for the integrated demonstration of the primary processes selected initially (mediated electrochemical oxidation [MEO], molten salt oxidation [MSO]).

Ability to Implement

A candidate technology must have no obvious technical features or hazards that would prevent the process from being used (demonstrated) at LLNL. The technology must have a reasonable probability of success; there should be sufficient evidence that known engineering problems are being overcome and addressed. If possible, the technology should have proven use in related commercial applications (e.g., for hazardous waste treatment). The technology must have a credible chance of being accepted by the public and the regulators. The feasibility of applying the technology on a scale appropriate to a commercial waste processing plant should be evident.

Range of Application

Support technologies must be flexible to accommodate the differing requirements of the initial selection of primary processes, and to maximize the potential to properly prepare, handle, and stabilize materials from future primary treatment technologies. Preference will be given to technologies applicable to a substantial range in the composition and properties of the feed and residue. This is necessary because there is considerable variability within a given input waste stream, and also because the residues will depend in part upon the primary process employed.

Process Effectiveness

Support technologies must effectively handle and prepare feeds to meet input requirements of primary treatment processes and immobilize treatment residues. Preference is given to technologies that meet process and regulatory requirements while maximizing the fraction of waste feed that can be processed and minimizing the final waste volume.

Stage of Development

Technologies selected for demonstration must be bench-scale mature and ready for pilot-scale operation within one or two years. The selected technologies are considered emerging/innovative in the sense that they may require additional engineering development before demonstration ("emerging"), or they may be mature but never have been applied to radioactive wastes ("innovative").

Industry Interest

Preference will be given to technologies with sufficient interest to industry; e.g., technologies that sponsor collaborative development with DOE or EPA or that are in the process of commercializing the technology for application to either hazardous or mixed low-level wastes (MLLWs).

DOE/EPA Interest

Strong consideration will go to technologies that are currently or have been recently funded by DOE or EPA for research and development, demonstration, testing, or evaluation.

Waste Minimization/D&D

Technologies producing a minimum of secondary waste (i.e., volatilized compounds, cleaning materials, protective clothing) during operation and decommissioning are preferred. Technologies that result in a minimum of contaminated equipment are preferred.

General Considerations

Reduction of risk to operators, both industrial hazards and radiation exposure, is recognized as a concern and will be considered in technology selection. Additionally, operating and implementation costs (life-cycle costs) of candidate technologies are also a consideration; however, detailed cost information is generally not available at this level of evaluation.

4.3 Technology Assessment for Process Support Systems

This section summarizes support demonstration technologies evaluated in the MWMF. The focus is on the selection of fundamentally different approaches for accomplishing support operations that will significantly advance the state of currently employed technologies.

4.3.1 Feed characterization and preparation

The technologies listed below and described in Appendix A.1 involve characterization, handling, and preparation of feed material for the primary processes. In each of these areas, the availability of relatively mature, leading-edge technologies provides several options to be evaluated prior to technology selection.

Containerized waste characterization

Containerized waste characterization refers to noninvasive (nondestructive evaluation and nondestructive analysis) techniques for gathering qualitative information on waste container contents to determine appropriate methods for safely handling and treating the container contents. The following methods for container characterization were evaluated and are described in Appendix A.1.1:

- Generator knowledge
- Real-time radiography
- Active and passive computed tomography.

Waste handling and sorting

Waste handling and sorting refers to methods for segregating heterogeneous wastes into appropriate feed streams for the primary treatment processes. The following

methods for waste handling and sorting were evaluated and are described in Appendix A.1.2:

- Manual handling
- Teleoperated or telerobotic handling
- Automated handling.

Liquid/liquid phase separation

Liquid/liquid phase separation refers to separation of immiscible organic and aqueous constituents in an emulsion when concentration of organics may be too high for membrane or media-bed processes. For example, Trimsol-based cutting emulsions, widely used in machining operations, have rather high (~8%) oil content, which, once the surfactants are destroyed, renders liquid/liquid phase separation a preferred technology. The separation of immiscible liquid phases is distinct compared to other phase separations (gas/liquid, liquid/solid, gas/solid) in that the important density difference between the phases is usually very small, sometimes less than 0.1 g/cm³. Separation of phases with small density differences requires large equipment, application of large forces, or unique equipment geometries. The following methods for liquid/liquid phase separation were evaluated and are described in Appendix A.1.3:

- Gravity separation
- Centrifugal separation
- Interception (coalescers, flotation, ultrafiltration, and microfiltration).

Material transport

Material transport refers to the method for moving material between two processing areas, often through a noncontaminated facility area. The following methods were evaluated and are described in Appendix A.1.4:

- Bagged material transport
- Enclosed transport systems
- Bagless transport methods.

4.3.2 Final Forms

Final Forms accepts process residues from primary treatment and immobilizes them in order to meet various regulatory guidelines for final waste disposal. Final Forms expects to immobilize three principal types of residue. These are grouped for convenience under the terms mineral residue, salt, and volatiles. The technologies listed below are described in Appendix A.2.

Mineral residue

Mineral residue refers to oxides, nitrates, and other inorganic process residues. The following waste form technologies, described in Appendix A.2.1, have been assessed for immobilization of mineral residue:

- Polyphase ceramics
- Vitrification
- Phosphate-based ceramics.

Salt

Salt refers to NaCl, with a small amount of NaF and trace contaminants that result from the destruction of halogenated organic compounds. The following waste form technologies, described in Appendix A.2.2, have been assessed for immobilization of salt:

- Thermosetting polymer encapsulation
- Thermoplastic organic polymer encapsulation (polyethylene)
- Fly-ash/salt brick ("TIDE").

Volatiles

Volatiles refers to inorganic compounds volatilized during any primary or support process and subsequently trapped. Examples include Hg, AgCl and MoO₃. The following waste form technologies, described in Appendix A.2.3, have been assessed for immobilization of volatiles:

- Sulfur-polymer cement encapsulation/immobilization
- Grout.

4.3.3 Off-Gas Treatment

Off-gas treatment removes hazardous components from gaseous effluents of mixed waste treatment processes. At the MWMF, it consists of two major systems: the Facility Off-Gas Treatment, representing BACT, and Experimental Off-Gas Treatment. The BACT technologies are required to meet permitting requirements and are selected based on the expected effluents, not on the evaluation criteria presented previously. Although treatment at the source is usually the most economical, few off-gas sources in the MWMF are large enough for even minimum-size commercial treatment units. Therefore, the sources are dealt with as two groups: one requiring reduction of NO_x, and another requiring oxidation or removal of VOCs and/or CO. BACT catalytic processes are employed in either case, and the caustic scrubbing is provided for the removal of acid gases. At the end of the off-gas treatment train, the HEPA filters ensure that essentially no particles escape into the environment. They filter the entire facility exhaust, consisting of treated process off-gas, the enclosure gas (typically air), and the room air.

Experimental Off-Gas Treatment (XOG) comes upstream of the Facility Off-Gas Treatment. Two missions have been identified: destruction of NO_x, and methods for removing particulates from the process off-gas. The objective of the XOG treatment system is to demonstrate advanced, innovative technologies that minimize secondary waste as well as the feasibility and effectiveness of treatment at or near the source of the effluent. Three specific technologies being proposed for evaluation are listed below and described in Appendix A.3:

- Catalytic de-NO_x
- Advanced wet de-NO_x
- Metal HEPA filters.

4.3.4 General references

H. Holmes Burns, M. L. Meyer, "Evaluation of Treatment Technologies for Immobilization and Volume Reduction of Mixed Waste," *Proc. 1993 Mixed Waste Symposium* (Tuscon, 2/28–3/4), Westinghouse Savannah River Co. #WSRC-MS-92-143 rev. 1.

J. L. Mayberry, L. M. DeWitt, "Technical Area Status Report for Low-Level Mixed Waste Final Waste Forms," vol. 1. (U.S. DOE report DOE/MWIP-3, 1993.)

L. J. Jacobs, W. R. Penney, "Phase Segregation" in *Handbook of Separation Process Technology*, R. W. Rousseau, ed., John Wiley & Sons: New York, 1987.

R. A. Corbitt, "Wastewater Disposal" in *Standard Handbook of Environmental Engineering*, R. A. Corbitt, ed., McGraw-Hill, Inc.: New York, 1990.

W. B. Hooper, L. J. Jacobs, Jr. "Decantation" in *Handbook of Separation Technologies for Chemical Engineers*, P. A. Schweitzer, ed. McGraw-Hill Book Co.: New York, 1988.

W. Lutze, R. C. Ewing, *Radioactive Waste Forms for the Future* (North-Holland, 1988).

4.4 Results of the Technology Selection

4.4.1 Technologies for initial process demonstration

Support Process Selection. Table 3 lists the technologies selected for the initial process demonstration.

Table 3. Technologies selected for initial process demonstration.

Feed Preparation	Generator knowledge
Containerized waste characterization	Real-time radiography for organic volumetric fraction analysis
Waste handling and sorting	Telerobotic handling
Liquid/liquid phase separation	De-emulsification and gravity density separation
Material transport	Bagless transport methods
Final Forms	
Mineral residue	Polyphase ceramic
Salt	Thermosetting polymer encapsulation
Volatiles	Sulfur-polymer cement encapsulation
Off-Gas Treatment	
NO _x	Advanced wet DeNO _x Catalytic DeNO _x
Particulates	Metal HEPA filter

Feed Preparation. Generator knowledge, confirmed by real-time radiography (RTR), was chosen for containerized waste characterization. RTR is expected to provide the qualitative and gross quantitative information needed for container receipt and characterization during initial MWMF operations. Additional information that would

be provided by active and passive computerized axial tomography (CAT) scan would be extremely useful in a facility accepting waste with questionable traceability, and may be appropriate for evaluation as the technology is further developed. However, LLNL wastes are generally well characterized, and the container contents are represented on the waste requisition.

Telerobotic waste handling and feed preparation was chosen for deployment in the MWMF. Telerobotics provides the flexibility needed to increase or decrease the amount of automation or operator intervention according to task complexity. However, the telerobotic system will not preclude manual operations if required. Telerobotics provides an inherent backup in that it can be operated in a master-slave mode as required. Non-routine maintenance is expected to be performed manually.

Gravity and centrifugal separation remain as leading candidates for liquid/liquid separation. Expensive and complex disk centrifuges perform well on liquid/liquid separation and should be used where gravity separation is either too slow or imperfect. However, with proper antisurfactant, adequate gravity liquid/liquid separation in Trimsol-based cutting emulsions within acceptable time has been demonstrated. Therefore, de-emulsification and gravity settling have been chosen for separation of aqueous and organic constituents in emulsions. The process is simple, reliable, and inexpensive, and provides the flexibility to use the equipment for other process operations if required.

Storage and transport of materials between MWMF subsystems will use a variety of technologies, depending upon the form and quantity of the material being handled. As a general approach, bagless transfer methods will be employed for batch material delivery. Bagless transfer technology provides a great deal of flexibility in equipment arrangement within the facility, provides a clean upgrade path from manually guided systems to automated systems as funding allows, and minimizes enclosures required during transport that would contribute to egress problems and waste generation during development and demonstration (D&D) activities.

Final Forms. Ceramic waste forms very well satisfy the selection criteria. Ceramics are an excellent match to the mineral residue composition expected from LLNL mixed waste input streams. Two ceramics have been designed, one for low-mineral residue and one for high-mineral residue content. Mineral residue from waste streams are abundant in compounds used in the ceramic formulation. With blending of mineral residue, waste loadings in excess of 50 wt% are feasible. The ceramics have a high tolerance for variations in the residue compositions. The science and technology of ceramic waste forms is advanced. The method is probably the most effective immobilization scheme known: the resulting waste form is mechanically durable and extremely resistant to leaching. There are no known barriers to implementation, and LLNL has prior experience with ceramic waste forms. Equipment contamination is minimal, as are secondary wastes.

Presently, there exists no fully satisfactory method of immobilizing NaCl. Microencapsulation in polymers appears to be most effective. However, at the time of initial selection, it was difficult to make a decision between thermosetting and thermoplastic polymers. Both types appear to have favorable properties and same unresolved development issues. Based mainly on cost considerations, thermosetting

polymers were selected as the basis for conceptual design. However, from a technical viewpoint, thermoplastic polymers appear to have the edge, and at Preliminary Design Review they will be reassessed.

The elements in LLNL mixed waste streams that may be expected to form volatile compounds are generally difficult to immobilize. They tend to form mainly water-soluble compounds, with the notable exception of sulfides: All of the elements at issue form stable sulfides. Sulfur-polymer cement is therefore an excellent choice. Sulfur-polymer cement is 95% sulfur and is a thermoplastic polymer. It is applicable to all of the elements in question. Sulfur-polymer cement itself is a mature technology, though its application to waste immobilization is relatively new (moderately mature). It is effective and easy to implement. Although the same type of equipment is used as would be for polyethylene salt encapsulation, the sizes are much smaller because the volume of volatiles to be treated is quite small. Secondary waste is minimal.

Off-Gas. Selective catalytic reduction (SCR) of NO_x with ammonia has become BACT, but catalyst formulations continuously evolve, and periodically they need to be evaluated. The most active, poison-resistant, inexpensive, and environmentally friendly catalysts for MWMF high-temperature sources will be identified.

Acidic urea DeNO_x in advanced gas-liquid contactor is the only wet scrubbing technique that converts NO_x to N_2 and promises much higher NO_x destruction efficiency at much lower cost than standard packed column. It is ideal for low-temperature sources, such as MEO, where the same contactor also proved highly efficient regenerating nitric acid.

Advanced metal cleanable filters virtually eliminate secondary waste and associated costs, promise to meet HEPA standards, and are commercially available for demonstration in the MWMF.

Support Process Backup Selection

Feed Preparation. If the RTR system in LLNL's HWM department is not on-line prior to initial MWMF operation, a number of other radiography facilities exist that can provide similar information, although in a less convenient manner. In addition, it may be more difficult to identify small containers of liquids in containers of solids without the real-time capability. However, because the waste is being handled remotely following container opening, the additional information provided would be useful, but is not critical, to successful feed preparation.

Conventional teleoperation provides a backup to telerobotic operation and is a well understood and established technology. Teleoperation will be more tedious and does not provide a convenient upgrade path to more automated methods that are currently being investigated by EM-50 and industry.

Bagged transfer methods or enclosed transport mechanisms are both established methods for contaminated material transport and provide backup options if required. An enclosed transport mechanism is not as flexible as the bagless system, but is the preferred backup because bagged transfer can generate significant volumes of secondary waste.

Final Forms. As there remains some question concerning the suitability of encapsulating salt in a thermosetting polymer, a backup selection—thermoplastic

organic polymer encapsulation—was chosen. Thermoplastic (polyethylene) encapsulation is not subject to the risk associated with organic contaminants interfering in the cross-linking reaction and is the logical backup technology. However, thermoplastic encapsulation does require heavy equipment which is expensive and whose decontamination may present a challenge.

4.4.2 Technologies for future operations

Future process support selection Technologies that were eliminated from initial process demonstration do not meet the stated criteria to the extent the selected technologies did, but are considered viable candidates for demonstration in future operations. These are shown below in Table 4:

Table 4. Technologies considered viable as future candidates.

Feed Preparation	
Waste Characterization	Reverse geometry x-ray tomography Active and passive computed tomography by gamma spectroscopy
Feed Sorting	Autonomous sensor-based sorting
Transport and Storage	Modular transport systems
Final Forms	
Mineral residue immobilization	Phosphate-based “chemical” ceramics Vitrification
Salt encapsulation	Thermoplastic polymer (polyethylene) microencapsulation
Off-Gas Treatment	
Low-temperature plasmas	Promising but immature candidate technologies for removal of NO _x , VOCs, and PICs in off-gas streams; possible implementation in later MWMF demonstrations.
Direct catalytic decomposition of NO _x	Attractive but immature candidate technology for destruction of NO _x without reducing agents; possible implementation in later MWMF demonstrations.

4.4.3 Rejected technologies

During the selection process, the following technologies were rejected from consideration for demonstration in the MWMF. The principal reasons for initial rejection of these support technologies are as follows:

Liquid/liquid separation

- Coalescers can be easily plugged with solids, require prefiltration, and are subject to biological fouling.
- Ultrafiltration and microfiltration are variations of an impact or interception mechanism and are good for clarifying, e.g., by removing dilute oil from water. However, the dispersed phase can only be concentrated, not separated.
- Electroseparators use electrical charging methods to remove traces of dispersed water from crude oil; the technology is not needed because there is no need to clean or perfect feed streams (to this level) before they enter MWMF treatment processes.

Final Forms

- Grout: This is judged a relatively poor waste form for our residues when compared with available emerging technologies. (LLNL has a grouting capability as a part of HWM. This may be used to dispose of MWMF waste that is inappropriate for the MWMF technologies. Examples would include large metal parts found in a feed stream, and waste that arose from a failed primary or support process run and that could not easily be reprocessed. Such use of grouting would not, however, be part of MWMF operations.)
- Fly-ash/salt ("TIDE") brick for salt: The potential for leaching of hazardous or radioactive components of the salt makes this a poor choice for a salt waste form.

Appendix A. Process Support Technology

This appendix summarizes each of the support technologies evaluated for the MWMF. It provides a brief review of the technology, describes the purpose of its demonstration within the MWMF, assesses each technology relative to the selection criteria described in Section 4.2, and discusses issues associated with integration of that particular technology in the MWMF. All the technologies have been evaluated against the standard criteria, but have been written by a number of different authors. The summaries are not intended to be all-inclusive—many documents, reports, and briefings have been generated on each of the process' alternatives. Some individual technology discussions include specific references.

A.1 Feed Preparation Technologies

The feed preparation technologies described herein are divided into four technology categories. *Containerized waste characterization* (Section A.1.1) refers to noninvasive (nondestructive evaluation and nondestructive analysis) techniques for gathering qualitative information on waste container contents to determine appropriate methods for safely handling and treating the container contents. *Waste handling and sorting* (Section A.1.2) refers to methods for segregating heterogeneous wastes into appropriate feed streams for the primary treatment processes. *Liquid/liquid phase separation* (Section A.1.3) refers to separation of immiscible organic and aqueous constituents in an emulsion when concentration of organics may be too high for membrane or media-bed processes. *Material transport* (Section A.1.4) refers to the method for moving material between two processing areas, often through a non-contaminated facility area.

A.1.1 Waste container characterization

A.1.1.1 Generator knowledge

Overview of Technology

When trying to nondestructively determine the contents of a waste container, the first information that exists is generator knowledge. This information is obtained from the generator at the time the container is packed. At LLNL, this information is contained in the HWM requisition form required to ship the mixed waste to the on-site storage area.

Purpose for Demonstration in MWMF

Before a container is moved into the MWMF containment area, its contents need to be assessed to determine if it will be accepted, to determine proper feed preparation area and to identify the hazards contained within it. Additionally, it is of interest to determine the amount of solid organics within a container to assess the cost effectiveness of removing waste that cannot be processed to remove waste that can be processed. Generator knowledge about the contents of the containers will be able to perform these functions in a limited way. The use of generator knowledge, coupled with subsequent waste characterization, will determine how well typical waste conforms to the drum requisition or drum content code.

Technology Assessment to Criteria

Appropriateness for MWMF

Generator knowledge can give much information about the contents of a waste container if the generator is diligent about reporting contents.

Ability to Implement

There are no impediments to use of this information for LLNL on-site wastes. In a typical DOE mixed waste facility, it may be difficult or impossible to retrieve this

information. However, correlation with NDE data from similar LLNL drums may provide a basis for establishing expected contents of these unknown containers.

Range of Application

This is likely broadly applicable to wastes stored aboveground in containers. It is likely not applicable to wastes that have been buried.

Process Effectiveness

In general, the generator information describing the mixed waste stored at LLNL is complete. In some cases, the information is not adequately descriptive. Also, some additional information not typically put on a waste requisition is required to determine amount of organics. It is likely ineffective for buried waste containers.

Stage of Development

Mature

Industry Interest

Unknown

DOE/EPA Interest

Unknown

Waste Minimization/D&D

Gathering information prior to accepting waste into the confinement area will allow rejection of unwanted containers. This will eliminate additional waste generation that would be caused during examination of unsuitable feed material.

General Considerations

None

Key Issues

Issues to be resolved before implementation

A pilot characterization study needs to be performed to verify generator knowledge.

Issues to be resolved in parallel to implementation and demonstration

None

Issues to be resolved as part of the demonstration

Verification of generator knowledge to identify differences between documentation and actual waste.

A.1.1.2 Waste container characterization using real-time radiography

Overview of Technology

A real-time radiography (RTR) system for mixed waste containers will output radiographs of each container to a video system. This information can be displayed to an operator on a video monitor where they can assess the contents of a container. This system also allows the operator to identify liquids by tilting the container under test. RTR systems are currently used in industry to identify defects in parts. Recent advances in radiographic image processing allow general categorization of materials into organics and inorganics.

Purpose for Demonstration in MWMF

Before a container is moved into the MWMF containment area, its contents need to be assessed to determine if it will be accepted, to determine proper feed preparation area and to identify the hazards contained within it. Additionally, it is of interest to determine the amount of solid organics within a container to assess the cost effectiveness of removing waste that cannot be processed to obtain waste that can be processed.. RTR will be used to supplement waste requisition information to make these determinations and facilitate properly handling of incoming feed material. RTR can also determine if free liquids exist within containers of solid waste. Demonstration of RTR for nonintrusive waste characterization, coupled with subsequent waste characterization data, will determine the performance envelope of RTR for identifying hazards and material properties of waste in unopened containers.

Technology Assessment to Criteria

Appropriateness for MWMF

Waste characterization is a vital component of operating an integrated waste-treatment facility. Validation that waste meets waste acceptance criteria and identification of hazards within waste containers is important to safe operation of the feed-handling systems.

Ability to Implement

Systems have been implemented at several DOE sites and there are now commercially available systems for whole-barrel scanning.

Range of Application

RTR is expected to be widely applicable to mixed low-level waste container characterization. Where higher levels of radiation have necessitated lead lining of barrels to protect operators working around waste containers, the level of energy needed to penetrate the lining may limit the effectiveness of some x-ray systems.

Process Effectiveness

The information provided by RTR is expected to provide significant insight into actual drum contents and their condition. An RTR system coupled with generator knowledge is expected to provide sufficient characterization to properly route

containers within the facility and to identify potential hazards, including unpunctured pressure cylinders and liquids in closed containers.

Stage of Development

The technology is well understood and commercial systems are available. The application of the technology for quantitatively identifying organic versus inorganic fractions and potential hazards for processing needs to be evaluated. This primarily involved additional image processing and several companies are advancing the state-of-the-art for luggage surveillance.

Industry Interest

Unknown

DOE/EPA Interest

RTR is used at several DOE sites for nonintrusive examination of barrels.

Waste Minimization/D&D

Gathering information prior to accepting waste into the confinement area will allow rejection of unwanted containers. This will eliminate additional waste generation that would be caused during examination of unsuitable feed material.

General Considerations

None

Key Issues

Issues to be resolved before implementation

None

Issues to be resolved in parallel to implementation and demonstration

The level at which the organic portion of the solid waste can be determined will be evaluated, as well as the ability to identify hazards within the containers.

Issues to be resolved as part of the demonstration

Validation of the performance and throughput of the system.

A.1.1.3 Active and passive computed tomography

Overview of Technology

Active and passive computed tomography (A&PCT) uses x-ray or gamma-ray absorption information to calculate the attenuation coefficients of material inside closed containers. It then uses this information coupled with passive measurements to determine which, if any, isotopes are contained within the container, their strength and their location. The attenuation information can also be used to determine material type since different materials have different absorption values.

Purpose for Demonstration in MWMF

A&PCT would be used within MWMF to identify the different waste stream components within a waste container and to identify any isotopes within the container that might be a hazard. The demonstration of A&PCT would greatly enhance the amount of information available on incoming waste material. It would be particularly valuable when the waste requisition describing the contents is unavailable, as in retrieved buried waste.

Technology Assessment to Criteria

Appropriateness for MWMF

The technology is appropriate for application when it matures.

Ability to Implement

Massive amounts of data are generated during this process and existing systems are extremely slow. Systems under development show promise to increase throughput and to provide excellent tools for operators to use when reviewing the data. While implementation is possible, a system deployed at this time would likely not be representative of the capabilities of systems that would be used in an actual facility.

Range of Application

The range of energies available for use with this technology make it extremely flexible and broadly applicable to expected waste containers.

Process Effectiveness

Existing systems are very effective at identifying categories and, in some cases, compositions of items within the container. The amount of radioisotopes can also be determined with a higher degree of certainty than with other methods.

Stage of Development

Although A&PCT would be valuable for identifying waste components within the facility, it is still an immature technology. The types of waste stream it can measure are the denser inorganic materials. Accurately measuring the lighter organic material is requires lower energy x-rays and much longer scan times. The current scan times are too long for the throughput required for this facility. Also, the automatic conversion of x-ray absorption information to material type has not been performed.

Industry Interest

There is industry interest in collaborative development of this technology.

DOE/EPA Interest

DOE has funded development of this technology over the past several years.

Waste Minimization/D&D

Gathering information prior to accepting waste into the confinement area will allow rejection of unwanted containers. This will eliminate additional waste generation that would be caused during examination of unsuitable feed material.

General Considerations

None

Key Issues*Issues to be resolved before implementation*

Improving speed and creating a database of x-ray absorption to material type conversion.

Issues to be resolved in parallel to implementation and demonstration

Verification of the data interpretation system.

Issues to be resolved as part of the demonstration

Validation of the performance and through put of the system.

A.1.2 Waste handling and segregation

A.1.2.1 Manual operations

Technology Description

Manual waste handling has been performed in industry and DOE facilities using gloveboxes and enclosures as well as “bubble suits” and other operator protective clothing. Both methods could be applied to mixed waste handling. Operators, dressed in appropriate protective clothing, would sort materials into feed-categories prior to feed conditioning steps. Manual operations provide the greatest flexibility for recovering from unexpected events, although it may place the operator at risk.

Purpose for Demonstration in MWMF

Manual waste handling is not recommended for demonstration in MWMF. However, manual operations are recommended for nonroutine maintenance and error recovery tasks. Although engineering pilot systems to ensure the success of remote maintenance operations has not been demonstrated to be a mature technology, equipment can be engineered to reduce risks to operators during maintenance activities. Engineering for ease of maintenance will lead to a better understanding of the engineering required to build a full-scale facility.

Assessment Relative to CriteriaAppropriateness for MWMF

Manual waste-handling operations, although an option, would lead to higher operator risks and waste generation greater than with remote operations. Manual non-routine maintenance is expected to reduce both cost and waste generation at this stage of technology maturity.

Ability to Implement

Manual operations can be implemented.

Range of Application

Manual handling has broad applicability where the range of motion and item weights do not exceed operator capacity when working through gloveports or in protective clothing.

Process Effectiveness

Due to the nature of waste-handling operations, manual handling poses hazards that are fundamentally more dangerous than production operations. Often the material may have been dismantled using saws, knives, or torches, and can have jagged and sharp edges. These factors pose a risk for puncturing or cutting operator gloves during material handling and sorting. In addition, objects may be heavy or simply wedged in the containers requiring large loads to be applied to remove them. Operators will not have the arm reach required to acquire items in the bottom of most containers. Fixtures and tools can be used to mitigate some of these hazards. Grasping and handling will have to be accomplished using a standard set of “tools” to the extent practical.

Stage of Development

Very mature—past practice for radioactive material handling in DOE facilities.

Industry Interest

Unknown

DOE/EPA Interest

The DOE Office of Technology Development has invested resources over the past 3 years to demonstrate robotic waste handling technology as an alternative to manual waste handling.

Waste Minimization/D&D

Historically, these operations have resulted in operator exposure to radiation and industrial hazards, as well as significant secondary waste generation from protective clothing and decontamination operations. The additional hardware design, components, tools and equipment required to remotely maintain a pilot/ prototype system could adversely impact the D&D costs of the demonstration equipment and the facility.

General Considerations

None

Key Issues

Issues to be resolved before implementation

None

Issues to be resolved in parallel to implementation and demonstration

Equipment must be designed to ease manual maintenance in contaminated environments.

Issues to be resolved as part of the demonstration

Productivity of operators performing maintenance and predicted doses maintenance personnel would be exposed to in a full scale facility will be assessed to establish the basis for manual versus remote maintenance in a full-scale facility.

A.1.2.2 Remote waste handling and segregation

Overview of Technology

Remote operations have traditionally been performed by several classes of master-slave manipulators including teleoperators, telemanipulators, and telerobots. Teleoperators provide one-to-one replication of operator motions (and forces) in a remote environment for the performance of a task. Telemanipulators are also operator controlled, but have electronic or computer augmentation to provide position and force offsets, scaling, or other operator enhancements. Telerobots can be operator or computer controlled, with some operations performed under operator control and more routine operations (often tool changing) performed under robot control. Telerobots are an enhancement to traditional master-slave manipulators that have been used to perform similar handling operations in DOE facilities for decades. While master-slave manipulators require an operator to control every action, telerobot systems increase productivity and relieve the tedium of repetitive tasks by providing robotic functions. System operators can generate programs that use sensor information to control the slave arm, as well as use the arm in simple record and playback sequences.

Purpose for Demonstration in MWMF

Telerobotics provides an alternative to manual handling through gloves or in protective suits/clothing and increases productivity over traditional master-slave systems. Remote operations will be required in typical DOE mixed waste facilities for reducing risks to operators and improving operations. Demonstration in the MWMF will determine system effectiveness and operator productivity while performing representative tasks. This information will be needed to feed the design and sizing of full-scale facilities.

Technology Assessment to Criteria

Appropriateness for MWMF

The application of remote handling technology reduces risks to operators posed by radiation, hazardous materials, and industrial hazards including heavy lifting and handling of sharp waste items. Telerobotics improves efficiency of remote operations and provides a clean upgrade path to fully automated systems as technology advances.

Ability to Implement

The technology is well understood and technical risk during engineering and implementation is low.

Range of Application

Telerobotics is broadly applicable to waste handling, sorting, and initial size-reduction tasks. It can also be applied to error recovery, decontamination, and remote maintenance of properly engineered systems.

Process Effectiveness

Teleoperation has been shown to be effective in many remote handling operations. Bench-scale telerobotic demonstrations have shown potential to improve productivity over teleoperated systems.

Stage of Development

The Robotics Technology Development Program has demonstrated the use of telerobotics in remote opening of waste bins and drums, size reduction, waste segregation, and waste sorting.

Industry Interest

Potential industrial partners are available for collaborative efforts to commercialize the technology for wider DOE use.

DOE/EPA Interest

The DOE Robotics Technology Development Program has demonstrated the use of telerobotics in remote opening of waste bins and drums, size reduction, waste segregation, and waste sorting. Development and demonstrations in this area are currently underway through DOE funding.

Waste Minimization/D&D

Remote operations reduce secondary and tertiary waste generation associated with operator protective clothing and decontamination operations required to reduce background radiation when manually handling wastes.

General Considerations

In systems analyses performed for planned DOE facilities, life cycle costs have been shown to be positively impacted by reducing the number of operators required to perform a task and reducing waste-disposal costs.

Key Issues

Issues to be resolved before implementation

None

Issues to be resolved in parallel to implementation and demonstration

To reduce implementation cost, a single control station can be used to control processing equipment and manipulators (slave arms in a master-slave system) in several unit operations. The ability to “multiplex” a single control station to several slave systems is a desirable, but not essential, issue to address in the system design. Based on advances in telecommunications, networking, and computer systems, this issue is expected to be easily resolved. The proper

integration of operator input devices and the manipulator arm is essential to achieve maximum system performance.

Issues to be resolved as part of the demonstration

Productivity of telerobotic systems in waste handling applications needs to be validated to assist in sizing of full-scale facilities. The impact of advances in sensor based control will be assessed to determine their potential impact towards fully automating feed receipt, characterization, segregation, and preparation.

A.1.2.3 Fully automated waste handling and segregation

Technology Description

Automated waste handling and preparation is accomplished through integrated handling, sensing and processing of waste feed materials. The integration requires sophisticated computer data interpretation algorithms to determine characterization information from often ambiguous and contradictory sensor information. The data interpretation system provides the required information to control waste handling and processing systems. A control program coordinates segregation and preparation equipment to prepare the feed streams according to the waste acceptance criteria of the process designated to receive the feed.

Purpose for Demonstration in MWMF

Automated data interpretation will assist facility operators in developing a better understanding of the characteristics of waste feed material and serves as a foundation for building faster processing systems. The automated system improves uniformity by removing subjective operator judgments from waste analysis, characterization, and preparation operations. A successful demonstration would have a significant impact on how the front end of future facilities would be designed and constructed.

Assessment Relative to Criteria

Appropriateness for MWMF

Automated waste handling and segregation is appropriate for demonstration in MWMF when the technology matures.

Ability to Implement

Current EM-50 funded demonstrations have not shown the technology to be ready for implementation in time for initial MWMF start-up and activation.

Range of Application

The range of application of this technology is primarily limited by the sensors and data interpretation needed to identify waste characteristics and determine appropriate system responses.

Process Effectiveness

At the current stage of technology maturity the system would not be effective without constant operator intervention.

Stage of Development

The Office of Technology Development has demonstrated several automated unit operations required to begin the automation of waste feed preparation. The maturity of the technology is at the proof-of-principal to bench-top level and is not ready for deployment as an integrated system at this time. Many of the improvements necessary are in soft technologies and may not result in large system cost increases when ready for deployment. However, significant development remains in sensor interpretation and data analysis.

Industry Interest

Unknown

DOE/EPA Interest

Significant EM-50 resources are being used to develop/demonstrate this technology.

Waste Minimization/D&D

Waste minimization, risk avoidance, and costs impacts are expected to be favorable.

General Consideration

Key Issues

Issues to be resolved before implementation

Improved sensor fusion and data interpretation algorithms need to be demonstrated prior to engineering development and implementation. Additional development is required in automating waste grasping, handling and initial size reduction tasks as well.

Issues to be resolved in parallel to implementation and demonstration

None

Issues to be resolved as part of the demonstration

Productivity and reliability of the task planning algorithms, size-reduction subsystem and automated waste characterization system will need to be evaluated at pilot scale prior to full-scale facility deployment.

A.1.3. Liquid/liquid separation

A.1.3.1 Gravity separation

Technology Description

Many designs are used for gravity separation in immiscible-liquid separators: horizontal or vertical vessels, troughs (API separators), and vessels with various internal configurations or parallel plates. The vessels may operate in a batch or continuous mode. The performance of gravity separators depends on two factors: the movement of dispersed-phase drops to the interface and the coalescence of the dispersed-phase drops at the interface. Each factor could be controlling. The coalescence is dependent on the purity of the phases and on the interfacial tension and may take from a fraction of a second to a few minutes to occur. The time gets shorter as the density difference between the phases increases, the viscosity of either phase decreases, and the interfacial tension increases. The presence of a surface-active agent or fine solids can interfere with or prevent the coalescing. Therefore, pretreatment or de-emulsification may include filtration, heating, or chemical destruction of surface-active agents. Long horizontal vessels provide the most desirable geometry for phase separation. In such horizontal decanters, the continuous phase flows perpendicular to the drops. This causes turbulence, which interferes with the settling process. Batch-operated gravity separators avoid the complications of turbulence in continuous separators. The distance (and the time) a drop must travel to reach a surface available for coalescence is made much shorter by closely spaced parallel plates placed, usually on an angle, into the separator. The parallel plates create individual flow channels, producing many separators in parallel. They also address the problem of turbulence by decreasing the hydrolic diameter for flow, which leads to laminar flow.

Purpose of Demonstration in the MWMF

Gravity separation, when its results are adequate, appears to be the simplest and least expensive method for liquid-liquid phase separation, a necessary step in a fully integrated treatment train, such as MSO. Due to a lack of moving parts, it is also virtually maintenance free, an important factor in servicing radioactively contaminated equipment.

Assessment Relative to Criteria

Appropriateness for MWMF

Trimsol™-based aqueous cutting emulsions with appr. 8% oil content constitutes one LLNL mixed waste stream. Its water content must be reduced to below 10% in order to feed it to MSO. This is attainable using gravity liquid/liquid phase separation.

Ability to Implement

There are no technical or safety reasons that would prevent gravity liquid/liquid phase separation from being used in the MWMF. The technology is mature and has hundreds of commercial suppliers from which to choose.

Range of Application

Gravity liquid/liquid phase separation is applicable to a very broad range of emulsions so long as either phase is present in substantial quantity; a high purity of either phase is not required. Whereas the same equipment can be used for a large number of emulsions; the time and/or throughput required to achieve a particular result may vary (see technology description).

Process Effectiveness

Gravity liquid/liquid phase separation is very cost effective and reasonably efficient so long as a high purity of either phase is not required. Depending on emulsion, the time and/or throughput required to achieve a particular result may vary (see technology description).

Stage of Development

Mature technology.

Industry Interest

Mature technology with hundreds of commercial suppliers from which to choose.

DOE/EPA Interest

No R&D other than normal testing is required.

Waste Minimization/D&D

An addition of a small amount (typically a fraction of one percent) of a de-emulsifying agent before phase separation may be required and usually ends up in the aqueous phase after separation. In addition, the aqueous phase may still contain after separation a few hundred or thousand ppm of organics (dissolved and/or dispersed) and would have to be sent to the waste water treatment facility. No other secondary waste is produced and the equipment is simple and easy to decontaminate.

General Considerations

Gravity separation is the simplest and the least expensive liquid/liquid phase separation option. It was proven adequate in our preliminary testing on TrimsolTM-based emulsions with appr. 8% oil content since thorough phase separation was not a requirement. The throughput, relatively low when gravity is used, can be increased by using a centrifuge, at considerably higher capital, maintenance, and operational costs. Because, however, the MWMF will operate only 8 hours a day, it leaves more than enough time for overnight gravity settling. The centrifugal separation is, therefore, viewed as a backup option.

Key Issues

None

A.1.3.2 Centrifugal separation

Technology Description

Mechanical centrifuges are used commonly for immiscible-liquid separation. The most common liquid/liquid centrifuge is the disk type design. The liquid flows in thin layers between the conically shaped disks. The lower-density liquid phase moves to the top of the channel between disks and toward the center of the centrifuge. The higher-density liquid moves toward the outside of the bowl but also exits at the top through a separate channel. Some solids can be handled with either periodic shutdown and cleaning or an automatic solids ejection by either parting the bowl momentarily or opening nozzles to eject solids.

Purpose of Demonstration in the MWMF

Centrifugal liquid-liquid phase separation is not recommended for demonstration in the MWMF for the purpose of separating aqueous and organic phases in Trimsol™ because simpler and less expensive gravity separation produces adequate results. Rather it ought to be viewed as a backup option should the requirements for phase purity and/or the throughput become higher in the future due to changes in regulations, primary treatment technology or the feed.

Assessment Relative to Criteria

Appropriateness for MWMF

Trimsol™-based aqueous cutting emulsions with approx. 8% oil content constitutes one LLNL mixed waste stream. Its water content must be reduced to below 10% in order to feed it to MSO. This is attainable using centrifugal liquid/liquid phase separation.

Ability to Implement

There are no technical or safety reasons that would prevent centrifugal liquid/liquid phase separation from being used in the MWMF. The technology is mature and has hundreds of commercial suppliers from which to choose.

Range of Application

This technology is applicable to a very broad range of emulsions if either phase is present in substantial quantity; a high purity of either phase is not required. Whereas the same equipment can be used for many emulsions; the time and/or throughput required to achieve a particular result may vary (see technology description).

Process Effectiveness

Capacities of disk centrifuges range from 0.01 to over 1 ft³/s. The specific gravity difference of the pure components should be at least 0.01, and the drop size of the dispersed phase should be at least 1 μm. Experimental results report removal of water from aviation fuel down to 0–5 ppm on feed streams of 15% water in the dispersed phase at machine capacities of 200 gpm.

Stage of Development

Mature technology.

Industry Interest

Mature technology with hundreds of commercial suppliers from which to choose.

DOE/EPA Interest

No R&D other than normal testing is required.

Waste Minimization/D&D

An addition of a small amount (typically a fraction of one percent) of a de-emulsifying agent before phase separation may be required and usually ends up in the aqueous phase after separation. In addition, the aqueous phase may still contain after separation a few ppm of dispersed organics (in addition to any dissolved organics) and would have to be sent to the waste water treatment facility. Some secondary waste (e.g., cleaning materials, protective clothing) may be produced as a result of required (scheduled) maintenance. Due to mechanical complexity, decontamination is also more complex than that of gravity separators.

General Considerations

Centrifugal separation is an efficient but expensive liquid/liquid phase separation option. Because of their high-speed moving parts, centrifuges are higher-maintenance items than gravity separators, a consideration made even more important by the possibility of radioactive contamination. Reliability can be a problem when centrifugal separation is used with inconsistent streams. All centrifuges must be maintained properly to insure balance and adequate system operation. The centrifugal separation is, therefore, viewed as a backup option.

Key Issues

None

References

W. B. Hooper and L. J. Jacobs, Jr. "Decantation" in *Handbook of Separation Technologies for Chemical Engineers*, P. A. Schweitzer, ed. McGraw-Hill Book Co.: New York, 1988.

A.1.3.3 Interception

Technology Description

Mixtures of immiscible liquids can be separated by an interception method analogous to mesh pads or fiber beds in gas/liquid systems. The mixture is passed through a dense bed of fibers or wire mesh and the dispersed drops contact with the media surface. Most systems are designed with media materials that are preferentially wetted by the dispersed drops. The dispersed material is held by the media until enough

material coalesces and large globules disengage from the media and separate by gravity. These devices are often referred to as coalescers.

Another impaction technique is flotation. Gas bubbles are used to intercept dispersed liquid drops and float them out of the bulk phase. The key to successful flotation is the selective adhesion of air bubbles to the material that is to be floated. Conditioning, collection and frothing agents are typically added. The actual separation, after the material has been made lighter by air-bubble attachment, is usually by frothing. The froth is then removed from the top of the flotation cell by a mechanical scraper.

Ultrafiltration (UF) and microfiltration (MF) membranes are another variation of an impact or interception mechanism. Several membrane configurations are available that differ in cost, membrane area/volume ratio, and resistance to fouling. Most UF and MF processes are operated in the cross flow mode where the feed and “concentrate” flow parallel to the membrane surface and only “permeate” or clean stream actually passes through the membrane. Pressures up to 100 psi are needed to promote permeation, and molecules that differ by a factor of ten in their molecular weight can usually be separated. Concentration polarization, plugging and fouling are factors that degrade membrane performance. To reduce concentration polarization, the membrane modules are operated under turbulent flow at high Reynolds numbers. Membrane fouling refers to the adsorption of material onto the membrane surface. Fouled membranes require chemical cleaning to restore their flux. These devices are good for clarifying continuous phase, for example, removing dilute oil from water. However, the dispersed phase can only be concentrated, not truly separated, because a strong continuous-phase velocity is required along the surface of the membrane to resuspend trapped dispersed-phase material to prevent fouling and blinding of the pores.

Purpose of Demonstration in the MWMF

Liquid-liquid phase separation technologies, such as coalescers and flotation, use interception as a means to promote coalescence in order to facilitate the gravity separation. They are not recommended for demonstration in the MWMF because simpler and less expensive de-emulsifying processes followed by gravity separation produce adequate separation of aqueous and organic phases in Trimsol™. They ought to be regarded as backup options should the requirements for phase purity and/or the throughput become higher in the future due to changes in regulations, primary treatment technology or the feed. They also tend to do more for purification of aqueous phase than for dewatering of the organic phase. The latter is particularly true of UF and MF processes, which often yield a virtually oil-free aqueous phase (permeate) while only marginally concentrating the organic phase. They may, perhaps, be demonstrated as waste water treatment technologies, but certainly not as feed preparation technologies in the MWMF.

Assessment Relative to Criteria

Appropriateness for MWMF

Trimsol™-based aqueous cutting emulsions with appr. 8% organics content constitutes one LLNL mixed waste stream. Its water content must be reduced to below 10% in order to feed it to MSO. This clearly renders UF/MF technology inappropriate

for the MWMF and leaves coalescers and flotation as possible enhancements to the gravity separation.

Ability to Implement

There are no unresolvable technical or safety problems that would prevent coalescers and flotation from being used in the MWMF. The technology is mature and has dozens of commercial suppliers from which to choose. However, coalescers are plugged with solids, require prefiltration and are subject to biological fouling; flotation uses compressed air, which strips VOCs or other volatile compounds from the feed, and may require complex pre- and aftertreatment. Ultrafiltration and microfiltration are high-capital cost items and may require considerable maintenance.

Range of Application

All liquid/liquid phase separation technologies based on interception are used with fairly dilute dispersions and small, less than 25- μm drop size. With even more difficult-to-separate emulsions (low interfacial tension, less than 1- μm drop size), dense media coalescers and membranes are sometimes effective. Chemical or heat treatment may be needed to break the emulsions by changing the interfacial tension followed by a conventional separation technique. For water dispersed in an organic emulsion, the electroseparators may be applicable.

Process Effectiveness

Coalescers and flotation remove drops down to 1–5 μm successfully. Separation efficiencies of greater than 90% were reported on flotation of 50–250 ppm oil concentration feed. When used for oil/water separations, ultrafiltration can produce a final concentrate containing up to 40% oil with water recovery of 95% or better.

Stage of Development

Mature technology; pre-engineered package systems are readily available. New membranes are continuously evolving.

Industry Interest

Mature technology with dozens of commercial suppliers from which to choose.

DOE/EPA Interest

No R&D other than extensive testing is required.

Waste Minimization/D&D

Flotation methods require the addition of small amounts of conditioning, collection and frothing agents that may end up in either phase after separation. An addition of chemical coagulants or flocculants produces chemical sludge. Coalescers can be plugged with solids, are subject to biological fouling, and, like fouled membranes, require chemical cleaning to restore their flux. This leads to secondary waste streams to be either treated further or disposed of as is. Some secondary waste (e.g., cleaning materials, protective clothing) may be produced as a result of required (scheduled) maintenance. Due to the overall complexity, decontamination is also more difficult than that of gravity separators.

General Considerations

Interception techniques are an efficient but expensive liquid/liquid phase separation option. They are not recommended for demonstration in the MWMF because simpler and less expensive de-emulsifying processes followed by gravity separation produce adequate separation of aqueous and organic phases in Trimsol™. They also tend to do more for purification of the aqueous phase than for dewatering of the organic phase. That is particularly true in the case of UF and MF processes yielding a virtually oil-free aqueous phase and yet only marginally concentrating the organic phase. They could be useful as waste water treatment technologies but not as feed preparation technologies in the MWMF.

Key Issues

None

A.1.4 Material transport

A.1.4.1 Bagged transfer of materials

Overview of Technology

In the MWMF, transfer of material will occur between confinement zones that are considered to be potentially contaminated across a zone considered to be free of contamination. One method of achieving effective material transfer is to provide a bagging procedure to transfer of materials from process enclosures to an enclosed container on a process transport vehicle. Bag-in/bag-out procedures and mechanisms have been the primary method for transport of contaminated materials in DOE facilities. Automated bag-out procedures have been demonstrated at several DOE sites and could be adapted for MWMF use.

Purpose of Demonstration in MWMF

Bagged transfer of materials provides an added level of containment and is the current technology in use. Remote operations will be required in typical DOE mixed waste facilities for reducing risks to operators and improving operations.

Technology Assessment of Criteria

Appropriateness for MWMF

Inappropriate due to increased radiation exposure and operator safety hazards.

Ability to Implement

There are no technical impediments to implementation of a bagged transfer system. Waste-minimization guidelines, ALARA and other regulatory guidelines may impede deployment of this option.

Range of Application

Bagging materials provides flexibility to accommodate primary treatment process changes.

Process Effectiveness

The technology is well established and is effective. In off-normal incidents, occasional contamination occurs during the procedure, but not on a routine basis.

Stage of Development

The technology in this area is well understood and technical risk during engineering and implementation is considered low.

Industry Interest

Unknown

DOE/EPA Interest

Unknown

Waste Minimization/D&D

Bagging materials adds to the secondary waste streams that are generated.

General Considerations

Life cycle cost/benefit analysis (including D&D and disposal costs) are not cost drivers except as related to cost of operators.

Key Issues

None

A.1.4.2 Enclosed transport of material

Technology Description

In the MWMF, transfer of material will occur between confinement zones that are considered to be potentially contaminated across a zone considered to be free of contamination. One method of achieving effective material transfer is to provide a confined pathway that exists at the same confinement level as the treatment processes. This would essentially be an enclosure that would run between each process. Similar technology has been used throughout the nuclear weapons complex and in the UK weapons establishment.

Purpose of Demonstration in MWMF

Enclosed transport provides an alternative to bagged or bagless transfer. Remote operations will be required in typical DOE mixed waste facilities for reducing risks to operators and improving operations. Enclosed transport systems may be appropriate or full-scale facilities when process flows and routing is static. Evaluation of

innovative methods of enclosed transport is appropriate at the pilot-scale prior to full-scale deployment.

Assessment Relative to Criteria

Appropriateness for MWMF

A confined material transport system reduces the risk of operator exposure by removing all contact with the transported material.

Ability to Implement

A variety of systems of this type have been used in other DOE facilities, including those at LLNL, LANL, RFP, and Y-12. The technology can be implemented.

Range of Application

The application of a confined material transfer system would not provide a high level of flexibility to accommodate primary treatment process changes.

Process Effectiveness

Enclosed systems can effectively transfer material. However, throughput does not warrant dedicated transport lines to each process and system utilization would be low.

Stage of Development

The technology in this area is well understood and technical risk during engineering and implementation is considered low.

Industry Interest

Unknown

DOE/EPA Interest

Unknown

Waste Minimization/D&D

It is also less desirable from a waste-minimization standpoint because the enclosure itself adds significantly to secondary waste production and D&D volume.

General Considerations

Life cycle cost/benefit analysis (including D&D and disposal costs) are drivers for additional costs.

Key Issues

None

A.1.4.3 Bagless transfer of materials

Overview of Technology

In the MWMF, transfer of material will occur between confinement zones that are considered to be potentially contaminated across a zone considered free of contamination. One method of achieving effective material transfer is to provide a bagless transfer of materials from process enclosures to an enclosed container on a process transport vehicle. This system is based on the “double-lid/double-door” concept and is expected to adapt commercially available systems.

Purpose of Demonstration in MWMF

Bagless transfer provides an alternative to manual handling and bag-out methods, reducing operator exposure and bag waste generation. Remote operations will be required in typical DOE mixed waste facilities for reducing risks to operators and improving operations. The reliability and flexibility of the system will be evaluated, as well as its potential for adaptation to automated delivery systems.

Technology Assessment of Criteria

Appropriateness for MWMF

Bagless transfer methods have been demonstrated for a variety of material transfer applications. The application to delivery of liquid and solid feed is innovative and appropriate for evaluation in MWMF. The potential benefit from a successful demonstration is reduced risk of operator exposure and reduced waste generation.

Ability to Implement

There are no major engineering hurdles expected that are likely to interfere with a successful deployment of the technology.

Range of Application

The technology is broadly applicable to delivery of discrete items and wet and dry bulk materials.

Process Effectiveness

Bagless transfer improves the efficiency of operation by reducing the number of steps in the operation.

Stage of Development

The technology is moderately understood and technical risk during engineering and implementation is considered low.

Industry Interest

A number of systems are available from industry for application.

DOE/EPA Interest

Several efforts have been funded both by DOE Energy Management (EM) and DOE Defense Programs (DP). Several test systems have been developed, but none is in use due to reduced process activity caused by changing DOE missions.

Waste Minimization/D&D

Eliminating the bag-in/bag-out operation greatly reduces the generation of secondary waste streams. Batch transfer using this technology is expected to greatly reduce D&D costs over contained transport systems (conveyors or carts).

General Considerations

In systems analyses performed for planned DOE facilities, life cycle costs have been shown to be positively impacted by reducing the number of operators required and reducing waste disposal costs.

Key Issues

None

A.2 Final Forms

Final Forms exists primarily to support the primary processes and only secondarily to demonstrate immobilization technologies. Accordingly, the three technologies selected were chosen for their immobilization effectiveness and general appropriateness in the MWMF context. Alternate final waste form technologies demonstrated in the future would not generally displace one of the basic three. Only if the new technology were found superior on balance (weighing immobilization effectiveness, safety, industry interest, cost, etc.) would it replace an existing scheme.

In the following subsections, the word “encapsulation” generally refers to microencapsulation of particulate waste, as opposed to macroencapsulation of large waste objects (piping, circuit boards, etc.). All of the technologies include protective garments and empty containers among their secondary waste streams, so these are not mentioned under the “Waste Minimization/D&D” criterion.

A.2.1 Mineral residue Final Forms

A.2.1.1 Polyphase ceramic waste form

Technology Description

Mineral residues are blended with additional mineral components and processed to form a crystalline ceramic material in the form of cylinders ~0.9 cm diam. × 0.9 cm tall. The overall composition is such that the final ceramic consists of several mineral phases. The phases are chosen such that the various compounds composing the waste are either a basic constituent of the phase or are soluble (in the solid state) in one or more of them.

The waste elements “partition” among the phases during processing. The basic composition and phase assemblage is designed to accommodate, flexibly, the input waste. The resulting material has little open porosity, is mechanically strong, and is very leach resistant. Standard ceramic processing methods are used: wet milling, calcining, granulating, uniaxial pressing, and sintering.

In our designs there are four major phases, with possible formation of small amounts of additional phases. The phase assemblage is similar to Synroc D. Maximum temperatures occur during sintering, ~1200°C. Blending of residues from different waste streams and/or primary processes increases efficiency but is not necessary. Waste loadings ~30 wt.% are predicted with blending.

Ceramic waste form is generally regarded as an alternative to glass waste form. In the United States, far more effort has been devoted to developing the latter.

Purpose for Demonstration in MWMF

Ceramic waste form is an ideal method of immobilizing the mineral residue wastes expected in the MWMF. Producing ceramic waste form in an integrated LLMW processing environment will provide a foundation for its subsequent use in full-scale treatment plants.

Assessment Relative to Criteria

Appropriateness for MWMF

Ceramic waste forms are an excellent immobilization method for the mineral residue residues expected from LLNL LLMW when processed by alternatives to incineration.

Ability to Implement

The technology is well understood, and the technical risk during engineering and implementation is low. Hazards to personnel and the environment are low. Regulators and the public are expected to find the technology acceptable.

Range of Application

Primary treatment technologies that are alternatives to incineration will generally produce mineral-forming residues (oxides, etc.), and ceramics are a natural means for immobilizing them. Because of the nature of the partitioning between the ceramic phases, the ceramics can immobilize residues of widely varying compositions.

Process Effectiveness

Ceramics are probably the most durable of all waste forms. With blending of wastes, high waste loadings are feasible.

Stage of Development

The technology is very advanced at the bench-scale level, with some experience (mainly in Australia) at a pilot-plant scale. Prior work has emphasized radioactive waste rather than waste from LLMW treatment.

Industry Interest

Industry interest (for hazardous, radioactive, and mixed waste) appears to be modest, but is expected to increase after the process has been demonstrated.

DOE/EPA Interest

Research and development on ceramic waste form technologies has been funded intermittently and at quite a low level, in the U.S. by DOE and DOD. Interest is increasing toward weapon dismantlement issues.

Waste Minimization/D&D

Secondary waste streams are minimal for this process. Principal process off-gas products are H₂O, CO₂, NO_x, and CO. Small quantities of some inorganic compounds will be volatilized and trapped. Waste water arises mostly from cleaning vessels and equipment. Contaminated equipment at D&D will be minimal, mainly parts rather than entire machines.

General Considerations

The ceramic processing capability should encounter minimal licensing difficulties. Hazards are minimal. Cost of construction and operation are modest.

Key Issues

There are no key issues. Some engineering development, aimed at the details of the processing to be used in MWMF, is needed.

References and Reviews

W. Lutze & R. C. Ewing, *Radioactive Waste Forms for the Future* (North-Holland, 1988).
V. M. Oversby, R. A. Van Konynenburg, W. E. Glassley & P. G. Curtis,
“Immobilization in Ceramic Waste Forms of the Residues from Treatment of Mixed
Wastes,” *Mat. Res. Soc. Symp. Proc.* 333, 285-292 (1993).

A.2.1.2 Vitrification

Technology Description

Mineral residues of the primary processes are blended with glass-forming materials, calcined and melted. The molten liquid is then cast as glass in a form suitable for disposal—often marbles ~0.9 cm diam. Elements composing the residue simply become part of the glass composition, exploiting the fact that glasses can be formed in a wide range of compositions. Many glass waste forms consists of two glassy phases intermingled on a submicroscopic scale (liquid-liquid immiscibility), and there are often minor amounts of crystalline phases present as well. The waste form is non-porous, strong and very leach-resistant, but may contain abundant cracks.

Purpose for Demonstration in MWMF

Glass waste form is an acceptable method of immobilizing MWMF mineral residue residues. Because vitrification is being extensively developed, tested and evaluated elsewhere, there is otherwise no particular benefit to using this technology as the main method of immobilizing the mineral residue. Adding a small vitrification capability, for use with high-silica residues (e.g., from scintillation cocktail vials), would be a logical complement to the ceramic process—and may be advantageous in a full-scale treatment facility.

Assessment Relative to Criteria

Appropriateness for MWMF

The overall compositions of glass waste forms do not match the MWMF mineral residue compositions very well, the latter being rather low in silica. Waste loading levels would therefore be modest. In addition, vitrification is so well developed and is being so widely tested that there is little motivation for demonstrating it in the MWMF.

Ability to Implement

The technology is well understood, and the technical risk during engineering and implementation is low. Off-gas problems are generally slightly more severe than for ceramic waste form, but are controllable. Hazards to personnel and the environment are low. Regulators would probably find the technology acceptable, but the public may be wary. LLNL has no experience with large-scale waste vitrification, but this could be remedied prior to construction.

Range of Application

Vitrification is readily applicable to our mineral residue wastes.

Process Effectiveness

Glass waste form is very leach-resistant and durable. Waste loadings would be lower than for ceramic waste form.

Stage of Development

Vitrification is an advanced technology at the bench- and pilot-plant scales in the U. S. It is used at the production scale in Europe, and the DWPF at Savannah River is near operation.

Industry Interest

There is considerable industry interest, both in using the vitrification to immobilize wastes and in manufacturing equipment for this purpose.

DOE/EPA Interest

Vitrification is supported extensively by DOE and DOD. In 1982, DOE selected vitrification as the principal process for immobilizing high-level radioactive waste at Savannah River.

Waste Minimization/D&D

Secondary waste streams are similar to those of ceramic processing: Off-gas is mainly H₂O, CO₂, NO_x, and CO; small quantities of inorganic compounds are volatilized and trapped; and there is process water from cleaning operations. Contaminated equipment at D&D will include a glass melter, a big piece of equipment.

General Considerations

Cost of a vitrification system for the MWMF has not been estimated carefully but is probably comparable to that of the ceramic system.

Key Issues

There are no key issues. A considerable effort on the part of LLNL personnel to familiarize themselves with the details of the technology would be necessary. (Hiring experienced individuals from outside LLNL would be an option.)

References and Reviews

W. Lutze and R. C. Ewing, *Radioactive Waste Forms for the Future* (North-Holland, 1988).

A.2.1.3 Phosphate-based “chemical” ceramics

Technology Description

Chemically bonded ceramics are formed at near room temperature by aqueous chemical reactions. The processing is similar to hydraulic cements, though setting times are slower. The important difference is that the bonding can be primarily covalent and ionic rather than Van der Waals and hydrogen bonding. In some designs, the material is subsequently heat-treated at moderate temperatures (~200–400°C). Attention has focused on phosphate-based systems for which natural mineral analogs suggest good stability. The waste form is strong but porous. Immobilization is a combination of chemical bonding and physical isolation. This is an emerging technology that may provide a good balance of immobilization effectiveness *vs.* cost. Negligible off-gassing is an advantage *vis-a-vis* high-temperature technologies, but leach resistance is unlikely to match that of ceramic and glass waste forms. The risk of waste components interfering with the process chemistry has not been fully evaluated. Tests with mineral residue wastes are encouraging.

Purpose for Demonstration in MWMF

Process demonstration on the pilot scale in the MWMF, and as a part of its integrated environment, would provide validation and engineering data for scaling to the treatment facility level.

Assessment Relative to Criteria

Appropriateness for MWMF

Demonstration of this technology would be appropriate in the MWMF. It would probably not be acceptable as the singular method of immobilizing mineral residue residues. Mineral residue residues from the treatment of absorbents (vermiculite, etc.) might be good candidates for chemically bonded phosphates, as would absorbent overpack that had become only very slightly contaminated.

Ability to Implement

There should be no barriers to implementation.

Range of Application

This has not yet been thoroughly studied. The technology *appears* to be broadly useful for the mineral residue wastes of the MWMF.

Process Effectiveness

Leach resistance is expected to be moderate—better than hydraulic cements but poorer than ceramics or glasses. Further data are needed before deciding whether to test the technology in the MWMF.

Stage of Development

This is an emerging technology. Bench-scale studies are in progress, but there is still a lot to learn.

Industry Interest

Current industry interest is moderate.

DOE/EPA Interest

DOE is funding exploratory studies at Argonne National Laboratory and elsewhere.

Waste Minimization/D&D

Secondary waste streams are negligible, as are ultimate decontamination and disposal problems.

General Considerations

None

Key Issues

The technology requires further development. The sensitivity of the process chemistry to waste stream variability is inadequately understood.

A.2.2 Salt Final Forms

A.2.2.1 Thermosetting organic polymer encapsulation

Technology Description

The material to be encapsulated, in our case salt, is blended with resins (monomers or low-molecular weight prepolymers), initiator, and stabilizers, and poured into a suitable container, such as a 55-gal drum. The polymerization and crosslinking reactions proceed. The chemistry is adjusted so that the reaction rates are slow enough that the heat of reaction, which is considerable, can be controlled and removed. The resulting waste form is a solid and durable polymer, incapable of melting, throughout which the waste is dispersed. Leaching is dominated by waste particles exposed to the leachant at the surface of the waste form. Interference of the polymerization reactions by components of the waste is a potential problem, particularly for waste streams having widely variable chemistries. In general, the thermoset chemistry must be evaluated (and possibly tailored) in the context of the waste being encapsulated. Equipment requirements are minimal. Process temperatures are low, but some polymer systems involve hazardous chemicals. Encapsulating nitrates or other oxidizers at high loadings is presently not recommended due to the potential of explosion. (The risks have not yet been adequately studied, so this view may change.) Thermosetting polymers are especially well-suited for the *macro*encapsulation of bulky waste, such as pipes and circuit boards.

The Conceptual Design Plan is to store the salt and encapsulate it when the accumulation warrants it—perhaps annually. A commercial subcontractor would do the encapsulation on-site in the MWMF.

Purpose for Demonstration in MWMF

Thermosets appear to be an excellent material for microencapsulation of MWMF waste salts (NaCl plus some NaF). Because microencapsulation of salts in thermoplastic polymers is being explored elsewhere, demonstration of the thermoset alternative in MWMF appears logical.

Assessment Relative to Criteria

Appropriateness for MWMF

Microencapsulation in thermosetting polymers is a viable technology for encapsulating MWMF salt. Equipment and floor space requirements are minimal.

Ability to Implement

There are no known technical barriers to implementation. Chemical hazards to personnel and to the environment depend upon the polymer system chosen, but are in all cases controllable. Regulators and the public may be concerned about these, and air permit applications will certainly be affected. Having a commercial team work in the MWMF on an occasional basis will be somewhat disruptive.

Range of Application

Thermosets are applicable to the MWMF waste salt, including the traces of hazardous and radioactive compounds present, though some tailoring of the thermoset chemistry may be needed.

Process Effectiveness

The process is effective in isolating the hazardous material, though it is not true immobilization. (There are no practical technologies that immobilize common salts in the sense of chemically reducing the leach rate to very low levels.)

Stage of Development

The technology is moderately well developed. It has been demonstrated at bench and pilot scales for salt, but is not yet widely or continuously used.

Industry Interest

Industry interest seems moderate. (It is higher for *macro*encapsulation.)

DOE/EPA Interest

DOE has funded experiments on this technology (Rocky Flats, Brookhaven, Hanford, INEL). Hanford has rejected its use. Pantex used thermosets, but this was regarded a short-term solution of an urgent problem.

Waste Minimization/D&D

High loadings (~50 vol.%) are feasible. Chemical vapors are the only significant secondary waste stream. Very little equipment needs disposal.

General Considerations

This technology was chosen early in the Conceptual Design. It was at that time thought that salt accumulations would be such that encapsulation could be done once after few years of operation, and less frequently thereafter. It now seems more likely that thermosetting encapsulation by a subcontractor would be done annually over a period of about a month. This routine disruption lessens the viability of this message. Thermoset encapsulation of salt could, of course, be made a part of the day-to-day operations of the MWMF.

Key Issues

The key issue is whether to proceed with the planned use of thermosets, or change the MWMF design basis to thermoplastic microencapsulation. This is now a Title I (Preliminary Design) decision. If thermosets are used, the polymer chemistry must be selected and adjusted to suit our wastes and the regulatory environment. Until this is done, the hazards will remain poorly defined. Air permitting may be affected.

A.2.2.2 Thermoplastic organic polymer encapsulation

Technology Description

The thermoplastic polymer, usually low-density polyethylene, is melted and continuously extruded from a twin-screw extruder. The material to be encapsulated, in our case salt, is introduced into the melt near the input end of the extrusion barrel. The operation of the twin screws disperses and blends the waste into the molten polymer. All this is standard polymer-processing technology. Typically, the extrudate is in the form of a long rod, which is chopped to form short cylinders of a size determined by regulatory testing considerations. As with other encapsulation methods, leaching is dominated by exposed particles at the surface. Ordinarily, the waste and polymer do not react chemically to any significant extent. Extrusion temperatures are ~120°C. The waste form is a durable polymer-waste composite. Loadings of ~50 vol.% are typical. Even with high loadings of nitrates, the material is essentially nonflammable and nonexplosive.

Purpose for Demonstration in MWMF

Thermoplastic microencapsulation is an excellent method of immobilizing MWMF waste salt. The processing would be done on regular basis, providing a demonstration in the integrated MWMF context.

Assessment Relative to Criteria

Appropriateness for MWMF

Thermoplastic microencapsulation is well-suited to MWMF salt waste.

Ability to Implement

There are no barriers to implementation. The mildly elevated temperatures will volatilize few waste compounds, so air permitting issues should be minimal. Regulators and the public should find the technology unobjectionable.

Range of Application

The method is applicable to most inorganic compounds.

Process Effectiveness

As with the thermosets, the process effectively isolates waste from the environment.

Stage of Development

The basic polymer technology employed is highly developed, and there is significant experience in applying it to the microencapsulation of salt.

Industry Interest

Industry interest seems moderate.

DOE/EPA Interest

DOE has a strong interest in the technology, which is actively being developed at Rocky Flats and ORNL.

Waste Minimization/D&D

Secondary waste is limited to very small amounts of process off-gas. D&D entails disposing of the extruder, typically a fairly large item. Recycled polyethylene can be used, thereby effecting a waste *reduction*.

General Considerations

In comparison with thermosets, the operating scenario is quite different: Thermoplastic microencapsulation would be carried out on a routine basis—whenever enough salt is accumulated to warrant an extrusion run. Initial costs are higher (screw extruder and ancillary equipment), but operating costs of MWMF would be lower (no subcontracting).

Key Issues

The only key issue is whether or not thermoplastics should replace thermosets as the design basis for MWMF “immobilization” of waste salt.

References and Reviews

A. Block-Bolten, D. Olson, P.-A. Persson and F. Sandstrom, “Polyethylene Waste Form Evaluation of Explosion and Fire Hazards.” New Mexico Institute of Mining and Technology, CETR Report FR-91-03, 1991.

A.2.2.3 Fly-ash brick

Technology Description

“TIDE” has become the common name of a process that can be used to encapsulate toxic waste using ASTM Class C fly-ash.* Class C fly-ash exhibits the behavior of a hydraulic cement, reacting with water to form a calcium silicate hydrate. It tends to harden very quickly, a feature that is usually troublesome but not in this application. The fly-ash is blended with a small amount of water (~10–20%), waste and possibly inert material. The mixture is compressed in a hydraulic press to form a brick. The brick is subsequently cured for ~10 days in moist air. The resulting brick has good mechanical strength but is porous. It is therefore sealed with a polymer coating. An attraction of TIDE brick is that it uses a waste material, the fly-ash itself; however, the process requires a particular type of Class C fly-ash.

Leaching rates of water-soluble wastes incorporated into the TIDE bricks are limited first by the polymer coating. If the limits of the polymer coating are breached, rates are limited by pH stabilization and diffusion in the water filling the pores. Generally, no other chemical immobilization takes place.

* TIDE stands for the Technical Development Engineering Company, Albuquerque, NM. The process is also known as the Phoenix Ash Technology (PAT).

Purpose for Demonstration in MWMF

TIDE brick is under consideration for immobilization of some hazardous wastes, and there is interest in testing it in an integrated treatment environment. It would be used to immobilize mineral residue, but we also evaluate it here for applicability to salt.

Assessment Relative to Criteria

Appropriateness for MWMF

TIDE seems generally inappropriate for the MWMF. It is a less satisfactory waste form than ceramic or glass, though cheaper. Encapsulation of salt in TIDE is unlikely to yield acceptable leach rates.

Ability to Implement

There are no barriers to implementation.

Range of Application

TIDE stabilization appears to be applicable to a broad array of mineral residue wastes, but the potential for waste components interfering with the TIDE chemistry has not been adequately studied. The applicability to salt is very dubious.

Process Effectiveness

Effectiveness has not been widely studied but is likely to be generally comparable to hydraulic cements.

Stage of Development

TIDE is in the early stages of development

Industry Interest

Unknown.

DOE/EPA Interest

There is little DOE funding at present.

Waste Minimization/D&D

Secondary waste streams are negligible. D&D includes disposing of a brick-making machine. The TIDE process uses a waste material, the fly mineral residue, to stabilize other wastes.

General Considerations

None

Key Issues

The process needs further development.

References and Reviews

A. Bruce King, "Evaluation of TIDE Solidification Technology for Mixed Waste Incinerator Bottom Ash." Report, National Environmental Technology Assessment Center, University of Pittsburgh, 1993.

R. D. Spence, C. L. Francis, I. L. Morgan and D. R. Trotter, "TIDE Stabilization of K-25 TSCA Incinerator Ash." Draft report, Oak Ridge National Laboratory, 1994.

A.2.3 Volatiles Final Forms

A.2.3.1 Sulfur-polymer cement microencapsulation

Technology Description

"Sulfur-polymer cement" (SPC) is elemental sulfur that has been reacted with organic compounds to stabilize the amorphous polymeric state of liquid sulfur. Physically, the material is a typical thermoplastic; in its interaction with wastes, its chemistry is much like elemental sulfur. Waste is blended with the SPC and screw-extruded in the same manner as is done with thermoplastic microencapsulation. Extrusion temperatures are ~140°C. The resulting waste form is durable and water-insoluble. It is essentially an encapsulant. It is especially suitable, however, for certain waste elements that form stable sulfides. Often these are the same elements that otherwise tend to form troublesome compounds that are both volatile and water-soluble. SPC is nonflammable.

Purpose for Demonstration in MWMF

SPC seems ideal for immobilizing inorganic compounds volatilized in high-temperature primary and final forms processes. SPC itself is a mature technology, but its use in immobilizing wastes is a fairly new development. Its demonstration and evaluation in the integrated environment of MWMF is worthwhile.

Assessment Relative to Criteria

Appropriateness for MWMF

SPC is an attractive emerging technology that is perfectly suited to immobilize MWMF volatiles. Re-volatilization of waste compounds should be suppressed by reaction with the sulfur.

Ability to Implement

There are no barriers to implementation. Very large quantities of molten sulfur are routinely and safely handled by industry; in comparison, MWMF quantities will be very small indeed. Permitting impacts should be minimal. Regulators and (perhaps after some explanations) the public should find the technology acceptable.

Range of Application

SPC microencapsulation is applicable to a very broad spectrum of waste. (It could, in fact, be used to encapsulate MWMF waste salt.)

Process Effectiveness

This is a very effective microencapsulation method.

Stage of Development

Although the use of SPC to encapsulate/immobilize waste is fairly new and still under development, the process is straightforward and should be of little concern. SPC for other purposes is a fairly mature technology. The polymer processing technologies needed are very mature.

Industry Interest

Producers of SPC are naturally interested in its development for waste disposal applications. Industries having waste of their own to dispose, or who are considering treating waste as a service, seem to be watching the development of SPC with interest.

DOE/EPA Interest

DOE is supporting some SPC encapsulation (macro as well as micro) at INEL and elsewhere.

Waste Minimization/D&D

Secondary waste streams are again minimal. The screw extruder, which must be disposed of upon decommission, would be fairly small (much smaller than the extruder needed for polyethylene encapsulation of MWMF salt).

General Considerations

Cost is modest, being dominated by the purchase of a small screw extruder. SPC itself is inexpensive, and the quantities required in MWMF almost negligible.

Key Issues

No key issues have been identified.

References and Reviews

A. van Dalen and J. E. Rijpkema, "Modified Sulphur Cement" (Commission of the European Communities, publication no. EUR 12303, 1989).

G. R. Darnell, W. C. Aldrich and J. A. Logan, "Full-scale Tests of Sulfur Polymer Cement and Non-radioactive Waste in Heated and Unheated Prototypical Containers." Idaho National Engineering Laboratory informal report, no. EGG-WM-10109, 1992.

A.2.3.2 Grout and other hydraulic cements

Technology Description

Hydraulic cements include Portland cement, gypsum cement (plaster of Paris), slag cement, and polymer-modified cement. Grout is a pumpable hydraulic cement. It contains more water than typical Portland cements, and often contains additives such as clay to increase the retention of hazardous chemicals and radionuclides. Leach resistance is low compared with ceramics and glasses but is satisfactory for some purposes.

Purpose for Demonstration in MWMF

Grout would encapsulate large objects (pipes, etc.) from Feed Preparation.

Assessment Relative to Criteria

Appropriateness for MWMF

Conceptually, grout is appropriate for the above purpose. LLNL Hazardous Waste Management has a grouting capability, however, so the local duplication seems unnecessary. Also, the process is adequately mature such that further demonstration is unnecessary. Because of their relatively low leach resistance, hydraulic cements are deemed inappropriate for the immobilization of MWMF treatment residues.

Ability to Implement

There are no barriers to implementation.

Range of Application

For the above purpose, grout is widely applicable.

Process Effectiveness

Effectiveness is satisfactory for the purpose of encapsulating large objects.

Stage of Development

The technology is very mature.

Industry Interest

Hydraulic cements are widely used for waste solidification and encapsulation.

DOE/EPA Interest

Waste Minimization/D&D

Secondary waste streams are minimal, as are D&D problems.

General Considerations

Given the maturity of the technology and the local capability, little purpose would be served by adding a grouting capability to the MWMF. If large objects are to be encapsulated in the MWMF, thermosetting polymers seem a more rational scheme.

Key Issues

None

A.3 Experimental Off-Gas Treatment

The following technologies were evaluated for experimental off-gas treatment (XOG). In all cases, best available control technologies will be used to process effluents from the XOG system. These technologies are candidates for evaluation because they show promise for significantly increasing the effectiveness of, decreasing the secondary waste generated by, or decreasing the cost of off-gas treatment.

A.3.1 Cleanable metal HEPA filter

Technology Description

Standard HEPA filters are used extensively throughout the DOE complex to prevent airborne contamination. The filters, which are made of glue and glass-fiber paper, are subject to structural damage when exposed to high air flows, shock waves, high temperatures, high humidities, and heavy particle deposits; therefore, they require costly gas conditioning and monitoring. Because HEPA filters cannot be cleaned, they are periodically replaced; thus, waste handling determines the overall DOE HEPA costs. LLNL, in cooperation with Pall Corp. and Memtec Corp., has developed a high-efficiency steel filter that can be clean in-situ by reverse air pulses. The filter media consists of a sintered steel fiber mat using 2-mm-diameter fiber. A standard HEPA configuration contains 64 pleated cylindrical filter elements in a 24 in. × 24 in. × 11.5 in. housing. This robust design can withstand back pressure pulses required for cleaning and other extreme conditions, and shows potential to exceed standard HEPA efficiency.

Purpose of Demonstration in the MWMF

To demonstrate feasibility and effectiveness of removing particulates from the process off-gas at or near to MWMF sources of the effluent and to test and demonstrate state-of-the-art, cleanable, stainless steel HEPA filters that minimize secondary waste.

Assessment Relative to the Criteria

Appropriateness for MWMF

The metal HEPA filter can result in significant cost savings and reduction of secondary waste streams within the DOE complex. While important to the treatment of mixed waste complex wide, successful demonstration will lead to significantly broader acceptability and additional cost savings.

Ability to Implement

There are no environmental, technical or safety reasons that would prevent advanced cleanable metal HEPA filters being demonstrated at LLNL. The added benefits to the MWMF would include simplified off-gas handling and the elimination of secondary waste associated with spent HEPA filters.

Range of Application

Metal HEPA filters are not subject to structural damage when exposed to high air flows, shock waves, high temperatures, or high humidities. They readily accommodate primary treatment process changes and do not require costly gas conditioning and monitoring.

Where a higher pressure drop is not objectionable, present (2- μ m fiber) metal HEPA filters can be used in all standard HEPA filters' applications. Metal filters based on 0.5- μ m steel fiber are expected to meet the pressure drop HEPA requirements as well, which will be demonstrated in 1994.

Process Effectiveness

The official DOE HEPA certification test of Memtec and Pall 2- μ m fiber filter cartridges, individual and assembled in the standard HEPA frame, concluded that they meet or exceed the penetration requirements of MIL-F-51068. However, the three-times-higher pressure drop precludes the qualification of these filters as HEPA filters. A succession of clogging and in-situ filter cleaning tests demonstrated that the steel filter could easily provide an equivalent life of at least 15 standard glass HEPA filters.

Stage of Development

Stainless steel fiber filters (2- μ m fiber) are commercially available from Pall Corp. and Memtec Corp. They represent adequately mature technology for immediate pilot-scale testing. The next generation of 0.5- μ m steel fiber filters, developed to meet pressure-drop HEPA requirements, will be ready for demonstration in 1994.

Industry Interest

Pall Corp. and Memtec Corp. are actively involved in the development and commercialization of cleanable metal HEPA filter.

DOE/EPA Interest

The work on cleanable metal HEPA filters at LLNL is supported by DOE's Office of Technology Development, EM-50.

Waste Minimization/D&D

Cleanable metal HEPA filters eliminate disposal and secondary waste problems.

General Considerations

While in-situ cleaning is nearly maintenance-free, the present system leaves a significant particle deposit on the filter after pulse cleaning, thus adding to the pressure drop across the filter. The ongoing development at LLNL, Pall, and Memtec addresses the high pressure-drop issue by improving the in-situ cleaning system and replacing the 2- μ m fiber with the 0.5- μ m fiber. The high-unit cost issue, typical with any new product, is also being addressed.

Key Issues

Further development of the in-situ cleaning system, commercialization of 0.5- μ m fiber filters, and significant unit cost reduction.

References

U.S. Military Standard MIL-STD-282, Filter Units Protective Clothing, Gas-Mask Components and Related Products: Performance Test Methods

U.S. Military Standard MIL-F-51068, Filters, Particulate (High-Efficiency Fire Resistant)

A.3.2 Selective catalytic reduction of NO_x with ammonia

Technology Description

Nitrogen oxides (NO_x) are removed most efficiently by Selective Catalytic Reduction (SCR), a technique widely used in Japan and Europe, which has lately become viewed as the Best Available Control Technology (BACT) in the USA. The process adds ammonia (directly or by in situ evaporation from the hydroxide) to an oxygen-containing exhaust stream that passes over the catalyst. SCR selectively reduces NO_x with an efficiency of 80 to 95%, depending on the nature of the feed. Performance depends on catalyst activity, the residence time, and the ratio of ammonia to NO_x in the exhaust. Depending on the catalyst formulation (the predominant SCR catalyst used today consists of vanadium pentoxide on a titanium dioxide support and is relatively expensive), SCR requires temperatures in the range 200°C to 400°C, residence times of 0.05 to 0.5 seconds, and is subject to tight control over the ammonia- NO_x ratio, the ammonia being a pollutant itself. Ongoing development aims at giving the process greater latitude to make SCR easier to operate and less costly. It also seeks to improve the catalyst's tolerance to various poisons.

Purpose of Demonstration in MWMF

To demonstrate feasibility and effectiveness of NO_x destruction at or near all future MWMF sources of the effluent, and, as they become available, to identify, test and demonstrate advanced, more effective catalyst formulations that minimize secondary waste.

Assessment Relative to the Criteria

Range of Application

There is a broad range of commercially available SCR catalysts of various shapes (pellets and honeycomb blocks, metal and ceramic, supported and monolith) and compositions (noble metals, transition metal oxides, Zeolites) to match a given combination of flow, temperature, composition, and potential catalyst poisons. However, there may be problems when HNO_3 vapor or NO_2 and H_2O are present in the NO_x mixture, due to possible salt formation in reaction with ammonia and plugging of the catalyst pores. For the same reason, a particulate filter and/or acid gas scrubber

may be required upstream of the catalyst. SCR, therefore, is ideally suited for high-flow, high-temperature sources usually associated with combustion.

Flexibility

SCR technologies are readily adaptable to accommodate primary treatment process changes as they can be easily updated as new improved catalysts are developed.

Waste minimization

Ammonia reacts selectively over SCR catalysts with NO_x or, in the absence of NO_x , with O_2 producing in both cases N_2 and H_2O . In this sense, SCR does not generate any secondary waste. However, catalyst activity declines with time or catalysts can be poisoned; then the spent catalysts become secondary waste. The only consumables in the SCR process are, therefore, ammonia and occasionally the catalyst itself.

Stage of development

SCR has become BACT in the United States and has been a preferred off-gas treatment in Europe and Japan for over two decades. It is still evolving as new improved catalyst formulations continue to appear on the market. SCR is a technology that is adequately mature for immediate pilot-scale testing.

Process Effectiveness

Up to 99% of NO_x destruction can be achieved with a proper match between a particular source and a catalyst. Honeycomb catalysts are compact, have low resistance to flow, and are effective even at very high space velocities, thus providing more advanced and economical NO_x abatement for the industry (as compared with traditional wet scrubbing methods).

Ability to implement

There are no environmental, technical, or safety reasons that would prevent SCR being demonstrated at LLNL. The process takes place at ambient pressure and temperature in the range of 200–400°C, produces no secondary waste, and particulate can easily be trapped upstream of SCR with, for example, a cleanable metal HEPA filter.

Industry Interest

There is considerable industry interest in improved SCR technology.

DOE/EPA Interest

The EPA is extremely interested in the development of improved catalysts.

General Considerations

SCR can be a very cost-effective technology, with proper catalyst selection. There are many cheap and effective metal oxide catalysts on the market that would provide the basis for very compact, maintenance-free processes with minimal energy consumption. However, certain metals, notably chromium, present in a number of formulations may cause a disposal problem in California.

Key Issues

All possible catalyst poisons from a given MWMF source need to be identified and the least poison-prone catalyst formulation needs to be selected. Spent catalysts need to be disposable in California.

A.3.3 Advanced wet scrubbing of NO_x

Technology Description

Scrubbing of NO_x with alkaline solutions is a commonly practiced off-gas treatment. While acid gases are scrubbed relatively easily, large and expensive absorption towers are required to overcome the low solubility of NO_x.

In the advanced wet scrubbing process, the alkaline solution is replaced with an aqueous acidic urea solution. Urea and its reaction products (N₂, CO₂ and H₂O) with nitrous acid formed from dissolution of NO_x are harmless, while alkaline solution scrubbing generates secondary wastes (nitrate salts) and causes packing fouling. The absorption column is, in turn, replaced with a compact, high-intensity gas-liquid contactor designed and built at LLNL. The contactor comprises a tank with a self-inducting impeller/aerator with a high gas-induction capacity. Its ability to recirculate sparingly soluble gases and to form a fine gas-liquid dispersion with high-shear-rate yields absorption rates unattainable in conventional packed absorbers. The new contactor offers two ways of eliminating NO_x from off-gas. Where nitric acid generation is desired, oxygen is allowed into the contactor to convert nitrous acid into nitric acid. Alternately, with urea solution the nitrous acid is destroyed as it forms.

Purpose of Demonstration in the MWMF

To demonstrate feasibility and effectiveness of NO_x control at or near MWMF effluent sources, and to test and demonstrate advanced, more effective NO_x wet scrubbing that minimizes secondary waste. The ability to perform nitric acid recovery and NO_x destruction while producing close to zero effluent will be demonstrated.

Assessment Relative to the Criteria

Range of Application

A broad number of commercial processes employ nitric acid in conjunction with metal refining, etching or finishing, or chemical nitrations; other processes employ heat to drive off nitrates. Within the DOE complex, nitric acid is routinely used for dissolution of plutonium oxide, and more advanced methods such as CEPOD/MEO are based on nitric acid electrolyte. The common off-gas characteristics of the above processes, such as a high fraction of NO₂ in NO_x mixtures, presence of nitric acid vapors, relatively low overall gas volume and, except for calcination, absence of particulates and near ambient temperature, make them good candidates for advanced wet scrubbing in a self-aerated gas-liquid contactor.

Flexibility (Adaptability)

Advanced wet scrubbing can be easily configured either for nitric acid regeneration or for NO_x destruction, or it can do both in a series of two nearly identical tanks.

Waste minimization

In an ideal arrangement (such as catholyte regeneration in the MEO process) advanced wet scrubbing consumes O₂ regenerating HNO₃ with an efficiency close to 99%, and it releases almost no effluent of any kind. During destruction of NO_x, the process consumes urea, releases CO₂, H₂O, and N₂, but still does not produce any secondary waste. Being acidic, the process is self-cleaning (there is no fouling of any kind), and possible particulate buildup is easily preventable with the use of cleanable metal HEPA filters upstream of the scrubber.

Stage of development

The theoretical and the experimental study of a self-aerated gas-liquid contactor, including optimum design and scale-up, was conducted in 1977 by Y. Zundeleovich. A recent nitric acid regeneration test at LLNL with a quarter-scale prototype of the MWMF unit proved successful, recovering 99% of the acid. The acidic urea destruction of NO_x in a packed column was patented in 1971 by A. Warshaw in the U.S. Patent 3 565 575, but the method only recently began receiving attention as virtually the only wet scrubbing process that does not generate secondary waste. This technology is considered mature at the bench scale and mature enough for pilot-scale testing in the next one to two years.

Process Effectiveness

The recent nitric acid regeneration test at LLNL with a quarter-scale prototype of the MWMF unit proved successful with 99% acid recovery. The acidic urea NO_x destruction is expected to be equally efficient.

Ability to implement

There are no environmental, technical, or safety reasons that would prevent advanced wet scrubbing from being demonstrated at LLNL. The process takes place at ambient pressure and temperature, produces no secondary waste, and particulates can easily be trapped upstream of the process.

Industry Interest

MWFM demonstration of urea process in highly efficient gas-liquid contactor should help industry to “rediscover” the benefits of NO_x wet scrubbing without producing secondary waste.

DOE/EPA Interest

The first LLNL report of 99% nitric acid recovery for MEO occurred at 30% CDR briefing and generated interest among DOE representatives.

General Considerations

In a 1990 review of dozens of reactive solvents for NO_x abatement, K. R. Jethani et al. concluded that an acidic urea system in a bubble column is economically the most

attractive for NO_x abatement. The self-aerated contactor is, in turn, far superior to either bubble column or packed column. Advanced wet scrubbing has promise of being a very cost-effective technology, with proper effluent selection.

Key Issues

The expected NO_x destruction efficiency with acidic urea using the self-aerated contactor needs to be demonstrated.

References

Y. Zundelovich, Power Consumption and Gas Capacity of Self-Inducting Turbo Aerators, *AIChE Journal*, 25, 763--773 (1979)

A. Warshaw, Chemical Construction Corporation Removal of Nitrogen Oxides from a Gas Stream, US Patent 3 565 575, 1971

K. R. Jethani, N. J. Suchak, J. B. Joshi Selection of Reactive Solvent for Pollution Abatement of NO_x, *Gas Separation & Purification*, 4, 8 (1990)

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